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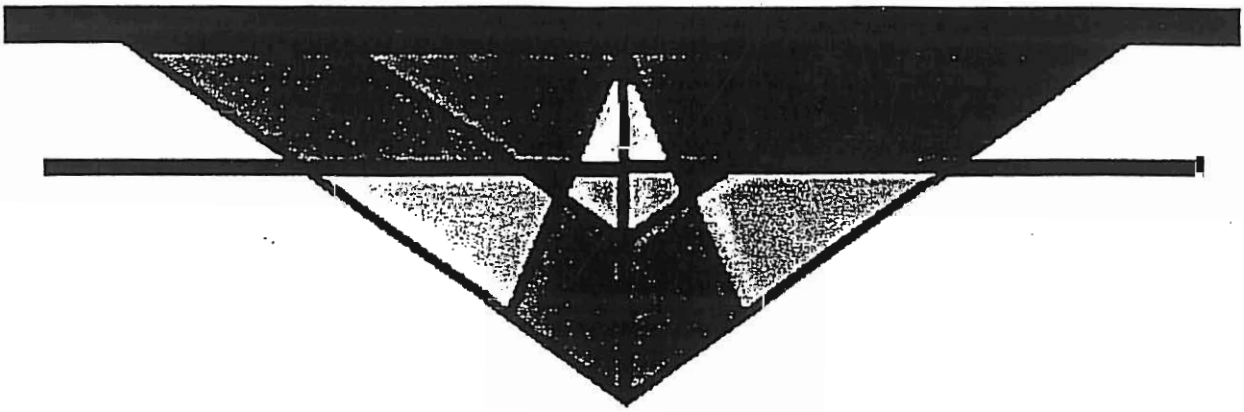
GLASS & STAINED GLASS

CONSERVATION WORKSHOP



JULY 27-31, 1998

GERALD R. FORD CONSERVATION CENTER
OMAHA, NEBRASKA

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INTRODUCTION

CONSERVATION AND RESTORATION OF STAINED GLASS AND GLASS OBJECTS

WORKSHOP SCHEDULE
FORD CONSERVATION CENTER
JULY 27-31, OMAHA

DAY ONE - MONDAY, JULY 27

9:00 - 9:30	Introduction to the Seminar (All Presenters)
9:30 - 10:30	Lecture: Glass Chemistry and Properties, I (Reedy)
Break	
10:45 - 12:00	Lecture: Glass Chemistry and Properties, II (Reedy)
Lunch	
1:30 - 2:30	Lecture: The History of Glass and Stained Glass (Reedy, Higgins)
Break	
2:45 - 3:45	Lecture: Glass Deterioration (Reedy, Higgins)
Break	
4:00 - 5:00	Lecture and Discussion: The Examination of Glass Objects (All Presenters)

DAY TWO - TUESDAY, JULY 28

9:00 - 10:30	Lecture: The Structure of Stained Glass Windows (Higgins)
Break	
10:45 - 12:00	Lecture: Structural Stability and Stabilization Options (Higgins)
Lunch	
1:30 - 2:30	Demonstration and Workshop: Disassembly (Higgins, Long, Reilly)
Break	
2:45 - 5:00	Lecture, Demonstration, and Workshop: Cleaning Glass (Higgins, Long, Reilly)

DAY THREE - WEDNESDAY, JULY 29

9:00 - 10:30	Lecture, Demonstration, and Workshop: Mechanical and Adhesive Repairs: Gluing, Infusion, and Hinging (Higgins, Long, Reilly) Part I: Mechanical Repairs
Break	
10:45 - 12:00	Part II: Adhesive Repairs (Higgins, Long, Reilly)
Lunch	
1:30 - 2:30	Lecture and Demonstration: Compensating for Losses: "New" Glass and Fabricated Fills (Higgins, Long, Reilly)
Break	
2:45 - 5:00	Lecture and Demonstration: Mold Making, Fills, and Filling (Higgins, Reilly, Long)

THURSDAY, JULY 30

Workshop: Mold Making, Fills, and Filling (Higgins, Long, Reilly)

Lecture and Demonstration: The Consolidation of Paint (Higgins)

Lecture: Cosmetic Reintegration: Overpainting, Inpainting, -ing Fills (Higgins, Long)

hop: Continue Workshop Projects (Higgins, Long, Reilly)

SCHEDULE

AY, JULY 31

e: Reassembly (Higgins)

e: Installation and Protective Glazing (Higgins, Vogel)

Workshop: Finish Projects and Clean-up (Higgins, Long, Reilly)

Continue to Finish Projects

Seminar Review, Questions, and Evaluation (Higgins, Long, Reilly)

Public Lecture:
"Color and Light: The Conservation of Stained Glass" (Higgins)
Followed by Reception, Joslyn Art Museum

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GLASS AND STAINED GLASS CONSERVATION WORKSHOP

JULY 27-31, 1998

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ACKNOWLEDGMENTS

The Glass and Stained Glass Conservation Workshop is sponsored by the Nebraska State Historical Society and generously funded by a grant from the National Center for Preservation Technology and Training of the National Park Service, Department of the Interior.

INTRODUCTION

The Glass and Stained Glass Conservation Workshop will be a five-day seminar on restoration and conservation of three- dimensional and stained glass objects at the Gerald R. Ford Conservation Center in Omaha. Designed chiefly for practicing objects conservators, stained glass professionals, and historic preservationists from the Midwest, who have few such training opportunities due to geographic and other constraints, the seminar will cover current cleaning, repair, and restoration techniques. Mary Clerkin Higgins, conservator of stained glass will be the primary presenter for the seminar and will give a public lecture about conservation on the final evening.

This training will apply up to date knowledge and techniques that are used in three related, but professionally segregated sub-specialties, to the conservation of glass objects The seminar is designed to substantially broaden the knowledge and exposure of all participants, while forging stronger ties between related specialties. The seminar will also present a needed learning opportunity for mid-career objects conservators and other professionals in the Midwest, who might not have been exposed to this information in their previous training or work environments.

The seminar will have broad application in preservation practice and contribute to a better distribution of knowledge in historic preservation because the techniques can be applied to flat glass of many types and objects as diverse as cathedral windows, desk lamps, architectural elements and art glass.

This training will offer the exciting opportunity for conservators in differing areas of specialization to share, compare and contrast similar techniques and materials in a workshop atmosphere. Attendees will learn the basics of glass chemistry, how glass deteriorates over time, appropriate cleaning techniques, how to glue breaks, how to mold and cast fills, and principles and techniques of cosmetic reintegration. Thus they will be able to continue to work with the restoration and conservation of stained glass and glass objects with more confidence and more sophisticated methods and materials.

The planned public lecture will also increase general knowledge of conservation practice among local museum professionals and the public.

Workshop Goal:

The workshop's goal is to increase the ability of objects conservators, stained glass professionals, and historic preservation professionals to successfully preserve cultural resources made of glass through increased knowledge of the chemistry, manufacture, restoration, and conservation of these materials.

Workshop Objectives:

1. After attending the seminar, participants will be able to identify the principles, materials, techniques, chemistry and approaches to treatment in glass conservation.

2. Participants will be able to apply the above knowledge to treatment of both flat glass and a variety of glass objects during the scheduled course lab sessions and to compare and contrast the approaches used in allied professions.

3. Participants will become familiar with the services and facilities of a complete laboratory dedicated solely to conservation practice at the Gerald R. Ford Conservation Center during the scheduled sessions.

COURSE INSTRUCTORS

MARY CLERKIN HIGGINS, is an artist and conservator in private practice who has worked in stained glass for over 22 years. In 1986 she established the Clerkin Higgins Studio. She is a member of the Board of Governors of the Census of Stained Glass in America and is actively involved in the field of conservation, lecturing, and writing on the subject. She is a Professional Associate of the American Institute for Conservation (AIC), as well as a former Secretary/Treasurer of the Objects Specialty Group of AIC. She is also an Associate Member of the International Institute for Conservation (IIC).

Ms. Higgins has conserved a number of notable works in stained glass from the 12th through the 20th centuries. Her practice includes both museum and architectural glass, with public institutions and private individuals as clients. She also creates new works. Her stained glass has been exhibited internationally and noted in articles and reviews.

CHANDRA L. REEDY, is an Associate Professor, Museum Studies Program, and Director, Art Conservation Research Ph.D. Program at the University of Delaware. She is responsible for designing and teaching courses in materials and technology of ceramics, glass metals, and stone; conservation research methods, experimental design, and data analysis; and for topics in Asian art history, museum studies, and historic preservation.

JULIE A. REILLY, has worked in objects conservation for the National Museum of American History, Smithsonian Institution; the Applied Archeology Center of the National Park Service; The Colonial Williamsburg Foundation; and the Henry Francis du Pont Winterthur Museum and Gardens. She served as Adjunct Associate Professor for objects conservation for the Winterthur/University of Delaware Program in Art Conservation and is currently an Adjunct Professor for the Museum Studies Department at the University of Nebraska at Lincoln. She is currently an Associate Director and Chief Conservator for the Nebraska State Historical Society where she directs the new Gerald R. Ford Conservation Center in Omaha, Nebraska.

DEBORAH L. LONG , currently is the Objects Conservator for the Ford Conservation Center. Deborah has worked in objects conservation at the H. F. Du Pont Winterthur Museum in Wilmington, Delaware for the last nine years, where she also served as adjunct assistant professor in objects conservation, for the Winterthur/University of Delaware Graduate Art Conservation Program.

Glass and Stained Glass Conservation Workshop

PARTICIPANTS LIST

Christine Birks

Stephanie Bruning

Suzanne Hargrove

Margaret Hernandez

Abby Hykin

Patricia Leavengood

Alexandra McCagg

Elizabeth Manship

Karen Messenger

Charlie Messenger

Joan Schiff

Pete Sixbey

Patricia Slothower

Linda Strauss

Neal Vogel

Glass and Stained Glass Conservation Workshop

SAFETY RULES FOR THE FORD CENTER LABS

The following rules are designed to ensure the safety of individuals and artifacts present in the laboratory spaces. Failure to comply with the rules listed below may prohibit you from participating in activities.

Smoking is not permitted in the Ford Center.

Food and drink are only permitted in the lunchroom. Gum and candy are not permitted in the labs.

Workshop participants are not permitted in the conservation laboratories without a designated Ford Center staff member present.

Never perform unauthorized work in the lab.

Horseplay is not allowed in the labs or in other areas where museum objects are likely to be found.

All tables and several chairs in the labs are fitted with wheels. Be careful not to lean on or push them.

Always be aware of objects and people present around you as you move through the laboratory space.

Treat every object as if it were an accessioned museum object of the highest value. Many of the objects are accessioned objects on loan from local museums.

Never leave your object unattended without posting a clearly legible "Object Below" sign and covering the object with a clear plastic cover.

Work spaces should be kept neat and free of clutter at all times.

No shorts, sleeveless shirts, or open-toed shoes are permitted in the labs. Clothing with loose fitting sleeves should be avoided. Loose jewelry and ties should be either confined or removed. Long hair should be tied back.

Safety glasses must be worn at all times in the conservation labs unless instructed otherwise by a Ford Center staff member.

Appropriate gloves must be worn when so instructed.

Hands should be washed preceding and following laboratory work.

Do not touch, smell, or taste any materials in the labs unless specifically instructed to do so.

Writing implements which utilize ink are not allowed in the lab. Only pencils may be used.

Do not leave any flammable materials in close proximity to heated apparatus. Never leave heated devices unattended.

Sharp blades must be closed or shielded when not in use. All sharp waste items, such as knife blades, should be placed in the sharp disposal can.

Immediately notify a Ford Center staff member of any damage or injury.

OUTLINES & NOTES

C.REEDY: NOTES FOR GLASS AND STAINED GLASS WORKSHOP, JULY 1998

THE "GLASSY STATE"

Glass is produced by cooling molten solids in such a way that crystallization does not occur and the material remains amorphous.

Glass = a supercooled liquid, contrasting with crystalline solids (where atoms occupy definite compositions in an ordered three-dimensional crystal lattice structure, with precise periodicity and symmetry).

Glass atoms are also arranged in a three-dimensional network, but without the periodicity, symmetry, and definite order of a crystal lattice.

Just below the melting temperature the glass must be cooled very quickly, giving crystals no chance to form and grow.

At freezing point most liquids change to a solid because the internal energy is minimal and the system is stable.

A supercooled liquid contains more heat energy than is appropriate for its temperature and it is thus more unstable.

But to reach the stable (crystalline) state, it would have to break the intermediate bonds in the liquid and make new bonds to form a crystal lattice structure. The bonds are too strong for this to happen. It gets more and more difficult as the temperature falls, and by room temperature it is essentially a liquid which has become too cold to freeze.

STRUCTURE AND COMPOSITION OF GLASS

GLASS STRUCTURE

Glasses have liquid-like structures, and are solutions (homogeneous mixtures of substances of dissimilar molecular structure) rather than chemical compounds with constituents combined in fixed amounts.

Thus glasses can be found with a wide possible variety of compositions and properties.
Major constituent = SiO_2, usually derived from sand. (The silica tetrahedron).

In the various forms of crystalline silica, each oxygen atom is shared by two silicon atoms: a structure is built up by the sharing of corners by pairs of oxygens.

Differences between crystal and glass:

Glass structure is more open

In glass the shared corners are arranged irregularly

Quartz sand will not melt until about 1700° C. Adding metallic oxides lowers melting temperature to 600-700° C by lowering viscosity because positively charged metallic oxides introduce extra oxygen into the structure, so it is no longer possible for every oxygen to be bonded to two atoms of Si. Those bonding to only one Si break the continuity of the network. The new bonds between them and the metallic ions are weaker.

At any given temperature the viscosity of a glass containing suitable metallic ions is less than that of pure silica. Thus the glass can be worked at a more reasonable temperature.

Oxides usually used to modify the structure of molten silica and disrupt the viscosity of the network: Na_2O, CaO, MgO, K_2O, PbO.

They may also be added to affect other properties as well as viscosity.

Silica = glass former -- has a three-dimensional crystal lattice, when heated enough it will break down and take on the random configuration of a liquid, but if a modifier (the metallic oxides) is added, and the melt is cooled too rapidly to allow crystallization, it will form a glass.

Result is an irregular three-dimensional network of silicon and oxygen atoms entrapping the modifier atoms.

Modifiers lower melting temperature, reduce viscosity of liquid glass, but some (Na, K) also diminish chemical durability of the glass by increasing its solubility in water.

Stabilizing compounds decrease solubility of soda and potash glasses to improve chemical durability. Lime or magnesia usually used.

GLASS COMPOSITION

1. Soda-Lime Glass

Na_2O is added as the metallic oxide.

CaO is added as a stabilizer in the form of limestone or as an impurity in the sand, producing soda-lime-silica glass.

Most common of all glass types, especially in the ancient world. Easily molded, can be blown thin, and easily drawn into fine threads.

Usual composition is about 75% sand, 15% soda, and 10% lime.

The high alkali content reduces the melting temperature to 725° C, but a high temperature will still be needed to reduce the viscosity enough to obtain a homogeneous melt and a transparent glass.

Some alumina (Al_2O_3) is usually added to improve chemical durability and to reduce tendency to crystallize.

Magnesia (MgO) helps decrease solubility along with the lime, and may also be present.

Compositions may vary but an overall balance is required. Too much soda causes glass to corrode too easily; with too much CaO tends to crystallize and is more susceptible to weathering; too much Al_2O_3 raises the softening temperature.

2. Potash Glass

When K_2O is substituted for Na_2O, the glass hardens more rapidly and at a higher temperature. Thus potash glass is less suitable than soda glass for molding techniques of ancient glassmakers.

3. Leaded Glass

PbO serves as a modifier to lower softening temperature. It yields a high density glass with a brilliance that was often sought after.

Natural sand contains some impurities such as CaO, so some additional ingredients could easily come from the sand.

THE CHEMISTRY OF GLASS COLORING

IMPURITIES VERSUS DELIBERATE COLORING

Main constituents of the glass are responsible for the color of the glass unless other agents are added deliberately. SiO_2, Na_2O, K_2O, and CaO produce colorless glass; small amounts of metallic oxides will produce color if present. This color may be accidental or intentional.

Iron impurities in the sand often provide unintentional color to glass. Ferrous (Fe^{2+}) ions = blue glass; ferric (Fe^{3+}) ions = yellow glass; combined ions = "bottle green" glass. Less than 1% is sufficient for this green effect. Romans added MnO_2 when iron was present = gray. Melting in a reducing atmosphere of a smoky fire increases proportion of ferrous ions = blue glass.

Intentional colors served to mask the natural green, brown, and purple tints produced by impurities in the raw materials. It may also have been the intent to imitate the colors of semi-precious stones.

The glassmakers must also control furnace conditions. Example: copper oxide in a reducing atmosphere (non-oxidizing and rich in carbon monoxide) = red glass; in an oxidizing atmosphere = blue or green.

COMMON COLORING AGENTS

Antimony	Yellow
Cobalt	Pale to dark blue
Copper	Blue, green, red, depending upon furnace conditions
Gold	Ruby red (when added as minute metallic particles to the glass, which is then reheated)
Iron	Untreated = green or brown. If combined with other metals (usually manganese or antimony) = yellow, amber, brown, or black
Manganese	Purple, rose-pink
Silver (sulfide)	Deep yellow
Tin	Opaque white

Many coloring agents can also be used as decolorizers = to neutralize the effects of any impurities present.

Opal and opaque glass = results when small proportions of crystals form as one of the components separates out of the melt during cooling, producing a small number of crystals within the glassy matrix. Effect varies from cloudiness to opalescence.

Tin oxide and antimony (as stibnite, Sb_2S_3) were often used as opacifying compounds.

Stibnite reacts with metal oxides in the glass melt to form antimoniates - $Ca_2Sb_2O_7$ = a white opal glass; $Pb_2Sb_2O_7$ = yellow opal glass. The only opacifiers used in antiquity.

Tin oxide was also added after the circa 4th century B.C.

TRANSFORMATION OF RAW MATERIALS INTO GLASS

BASIC RAW MATERIALS

Silica is usually sand, could be crushed quartz pebbles.

Major source of soda component is natural salts, occasionally from evaporation of water bodies or deliberate evaporation of sea or river water in pits (again, might get calcium or magnesium etc., as impurities).

Most often, plant ash (or wood ash) is also used for soda or potash glass depending upon plant composition.

Plant ash = Na_2O or K_2O, plus some CaO, MgO. Composition varies greatly from plant type to plant type, and for the same plants in different soil conditions.

Lime was often not deliberately added to ancient glass, but was an important constituent of the sand and/or alkali.

MAJOR STEPS IN TRANSFORMING RAW MATERIALS INTO GLASS

1. Mixing

The batch, including the glass former, modifier, and stabilizer, are initially mixed together as a dry powder. Excess glass from a previous melt of the same composition as the raw materials might be included (cullet). The craftsman might also add decolorizing agents, coloring agents, or opacifiers. Often the alkalis and some of the sand would be pre-heated and partially fused to form a "frit".

Problems: The alkali sources available to ancient glassmakers varied widely in composition, and contained a high percentage of material that could not be incorporated into the glass. These impurities were sometimes removed before melting.

Ash was crushed finely and boiled repeatedly, the extracts were ladled into earthenware bowls to settle after each boiling. The liquid was evaporated until crystallization occurred. These salt crystals were skimmed off, crushed, and sieved. Any remaining impurities are skimmed off during melting. But, the more purified the salt, the more the natural stabilizers were removed, affecting the durability of the product.

2. Melting

Melting of the mixed ingredients is done in a furnace (often divided into areas for fritting, melting, and annealing). The cullet will soften first, and its liquid helps the solid part of the batch to move around and mix with each other. Eventually a viscous liquid has formed and the entire mixture is fused together (1300-1500° C). The temperature will then be kept steady for several hours or is raised to improve mixing and remove bubbles and streaks. The homogeneous mixture of crystals takes on the properties of glass during this period. The temperature is then lowered somewhat to raise the viscosity for the fabrication stage.

3. Fabrication

Has to be completed during the short cooling phase (a few seconds to a few minutes). If more work is required after the highly viscous liquid becomes a solid, it must be reheated. Usual fabrication techniques are casting, drawing, blowing, and pressing. (3000 B.C. industries begin, 30 B.C. blowing)

4. Annealing

All finished glass is annealed to relieve any internal stresses to they will not be fixed into the solid glass. Glass is reheated to very near the softening point and held there for a few minutes, then is cooled at a controlled rate. If not done, fractures may result.

5. Finishing

Cold finishing = removal of excess glass by cutting, drilling, engraving, grinding, or polishing.
Hot finishing = reshaping and fusion sealing.

ANALYTICAL TECHNIQUES FOR STUDYING GLASS

COMPOSITIONAL ANALYSIS

Almost all ancient glass is soda-lime-silica glass. Analytical results usually are aimed at identifying other characteristics.

If the workability of glass of various compositions is known, a chemical analysis can be used to evaluate the choice of raw materials.

1. Elemental Analysis

By PIXE, XRF, SEM with XRF attachment, or by electron microprobe.

2. Isotopic Analysis

Lead Isotope Analysis

Pb-204, Pb-206, Pb-207, and Pb-208 are found in different proportions in different geological environments. Thus lead from different ore deposits can sometimes be distinguished from each other. Determining the fractional composition of the isotopes with a mass spectrometer is a technique that can be done on the lead impurities in glasses, or on any glass in which lead was added as an opacifier or colorant.

Problems: Can only group by common origin, cannot say where they are found unless have samples from all potential sources. If remelting of glass from a variety of sources occurred, will get incorrect groupings.

Oxygen Isotope Analysis

$^{16}O/^{18}O$ ratio varies in different materials. Glasses of different origins tend to have different ratios.

But there has been little work done on this as a provenance or authenticity tool.

ANALYSIS OF WEATHERING LAYERS

Obsidian can be dated by measuring its hydration layers. Applications to human-made glass have not yet been well developed. Need intact layers, periodicity, wet environment, corrodible glass.

HISTORY OF PRODUCTION METHODS AND AESTHETICS IN GLASS

PRODUCTION METHODS

- Carving
- Pressing in molds
- Lost wax casting
- Core forming
- Fusing and slumping
- Cane making
- Millifiori
- Blowing
- Blowing into molds
- Dip molds
- Machine pressing

SURFACE DECORATION

- Glued-on decorations
- Painting
- Enamelling
- Gilding
- Silvering
- Cutting
- Stippling
- Engraving
- Acid etching
- Threading
- Modelling
- Sandwiching
- Blobbing
- Cages
- Cameo
- Sulphides
- Flashing
- Staining
- Ink transfer printing
- Crimping
- Heat sensitive colorants
- Marbling

EXAMPLES OF SPECIALIZED PRODUCTS

- Mosaic glass
- Islamic glass
- Asian glass beads and inside-painted snuff bottles
- Roman products
- Venetian products
- 17th-19th century English glass
- Early American bottles
- Early American windows

DETERIORATION OF GLASS

ENVIRONMENTAL FACTORS

Dry environment = little decomposition.

Wet environment = soluble substances (alkalis) leached away, leaving a hydrated residue with a high silica content (shown by SEM with XRF). These crusts take a layered form (microscopically).

BACTERIAL ATTACK

Once decomposition begins, bacterial attack in the burial environment or prior to burial can accelerate the process.

Differential corrosion of glass from the same site may be due to bacterial attack effects.

FORMS OF CORROSION

High silica content = greater susceptibility to pitting corrosion. Weathering products form in these pits and associated cracks (often gypsum). An initial weathering stage. Later the layered weathering crust will form on the surface. Opaque crust with a gypsum corrosion product along with amorphous hydrated silica.

In leaching process: Alkaline network modifier ions are replaced in an ion exchange process by hydrogen or hydrogen-bearing ions. Alkaline earths may also be affected.

Fractures - take place at defects (microscopic fractures, flaws, scratches).

Devitrification causes opacity and tendency to fracture around crystals as they form.

Crizzling - Na glasses, Na leached out in moist environments, glass absorbs moisture, sodium carbonate forms a film on surface, dulling glass.

Weeping - K glasses, instead of forming a film, potassium carbonate appears as droplets on the surface.

Where SO_2 is present in the atmosphere, sulfides such as gypsum will form on the surface. The leaching process occurs faster in SO_2-rich atmospheres. Big problem with medieval windows in urban environments.

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA

The Census of Stained Glass Windows in America is a not-for-profit organization founded in 1979 to establish a record, both historical and pictorial, of architectural stained glass in the United States from the time of its first appearance. Windows of both American and European manufacture are included. The goal of the Census is to collect and disseminate artistic, historical, and technical information that will serve as a basis for study of this form of architectural embellishment. Windows frequently contain more specific references to the society that produced them than any other aspect of a building. Donors are noted in inscriptions, preferences for one kind of artistic style over another evident through the choice of studio, attitudes towards religion displayed by the type of imagery (or lack of it), and the wealth and social status of the patron conveyed by the lavishness of the commission. Serious study of all of these questions is contingent on locating and identifying these highly visible, but little understood aspects of our national heritage. To these ends the CSGA brings together experts from many different fields: specialists in the field of stained glass, architectural historians, art historians, museum professionals, and preservation experts.

For further information contact Virginia C. Raguin, CSGA Director
College of the Holy Cross, Worcester, MA 01610

March 1990

CONSERVATION AND RESTORATION OF STAINED GLASS:

AN OWNER'S GUIDE

prepared by

The Census of Stained Glass Window in America

This forty-page illustrated booklet covers all major questions in stained glass repair. Attention is paid to the importance of conserving an architectural art form that commemorates the religious, social, and economic history of a community. The dangers of over zealous restorations are reviewed. The text describes the essential elements of a stained glass window and includes a glossary of terms describing the varieties of windows and their technical structures. Simple steps are given to help plan a conservation campaign, such as suggestions for photographic and written documentation, points to be noted in examining the structural and decorative fabric of the windows, and questions to ask potential restorers. A section is devoted to specific cleaning and mending methods, those approved and those to be avoided. The owner is also given suggestions for adapting windows to alternate installations and purchasing security and insurance. The important and often controversial issues of the reinstallation of restored panels and the possible benefits and drawbacks of protective glazing are included. The booklet also includes a list of agencies dealing with conservation issues and a selected bibliography of works on historic stained glass.

The booklet is designed as an unbiased guide for the owner of architectural stained glass, and certainly no church or public building with stained glass windows should be without it. **The Old House Journal** calls the Owner's Guide **"a must-have for any person or group interested in restoring stained glass.** It should prove of special use for church and synagogue restorations." Several large Episcopal dioceses and Preservation Societies have made bulk orders of the guide so that all of the churches under their protection would have an informed guide.

The booklet is available through
Stained Glass Associates
Box 1531
Raleigh, NC 27602

Price $3.65 per copy (includes postage and handling)
Substantial discounts available for bulk orders
Telephone (919) 266-2493 or 833-7668

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA
HINTS FOR EFFICIENT SURVEY WORK

ORGANIZATION

1. It is absolutely essential to have a local contact who can schedule appointments with owners or caretakers of the buildings.

2. A team of three works efficiently. One "expert" can work with less experienced people in a very good relationship. Document gathering can be separated from the interpretation of the glass. Each person would transcribe information from the windows, especially inscriptions. The entire group can look at all the windows together and make judgments as to type of glass, subject matter, etc.

3. It is extremely important to ask the owners of the building for information. Contact persons who provide Xeroxes of written material (even newspaper clippings) about the building are invaluable. Often parishes have centenary publications and other commemorative booklets that describe the building of the church and the donors of the windows. Many have a church archivist or historian. Ask if these publications can be made available and if you could meet the individuals in these offices.

4. The team leader must review the data sheets as a whole. Often reference to the material provided by the contact person at the site will solve problems of difficult to read inscriptions or puzzling subject matter.

5. It is inevitable that surveyors will be asked questions about the condition of the windows and methods of repair.. These question can be met by stating that the Census is a not-for-profit organization and forbidden to enter into this area in specific cases. However, because the CSGA is aware of such concerns it has published Conservation and Restoration of Stained Glass: An Owner's Guide. Take one copy of the booklet with you on site, and give the church/building the flyer explaining how to obtain the booklet. See CSGA Constitution "The personnel of this organization will not offer any services in assessing monetary value of stained glass windows, nor will it recommend either restorers or methods of restoration. Nor will its publications or activities in any way whatsoever provide information relative to the sale or purchase of stained glass windows. The purpose of the organization is to record information, to make it publicly available, and to encourage the preservation and appreciation of the art in this country."

PHOTOGRAPHY AND OTHER EQUIPMENT

BASIC EQUIPMENT: Camera, (preferably with telephoto lense) tripod, tape measure, pen and pencil, data forms, flashlight, and binoculars.

CAMERA: It is essential to have a good camera that can be used without automatic features. A through-the-lens light meter is quite efficient, but you must be able to regulate shutter speed and size of apertures yourself.

FILM: ASA 200 or even ASA 400 Ektachrome slide film is quite adequate. A fast speed will allow many shots to taken without a tripod. However, in almost all cases it is necessary to use a tripod for some windows, and above all for details using a telephoto lense.

LIGHTING CONDITIONS: The ideal climate condition for photographing stained glass is a slightly overcast day. If you are photographing on a bright day try to time your photography work to take advantage of the side of a building in shadow. If you shoot into a sunlit window the glare of the light will distort the relationships among the colors and often confuse your light meter.

TEAMWORK: All survey teams should have one member who knows how to use a camera. If this person is the designated photographer, the others can concentrate on the written forms and work can proceed very efficiently. Take general views, but also take representative details that may be the most useful when attempting to identify the windows. It is recommended that some kind of working notes of the sequence of windows be kept, so that labeling of the slides becomes a routine job, not a guessing game.

DIRECTIONS FOR CENSUS FORMS

Remember that no survey will ever be flawless of absolutely complete. Given the almost TOTAL neglect of leaded and painted windows in architectural or historical surveys of buildings in America, it is essential this work begin. Most of the information to be recorded on the sheets is factual. The information is a measurement, an inscription, an address, or is derived from material found in local guidebooks, historical surveys, or in the archives of the buildings themselves. The drafting of a plan, numbering of windows, and a complete photographic record, where none existed before, render inestimable service . Inscriptions should be noted exactly as written, with misspellings, or peculiarities such as script, or upper or lower case. Copy the Signature exactly. Attribution should only be made on the basis of a studio list, a commission, or bill of sale (note this in Bibliography). If conjecture, indicate origin of opinion, such as the researcher's name. Judgmental issues are more problematic. Use a question mark if the decision is conjectural.

TYPE OF GLASS AND TECHNIQUE

Opalescent: Glass typical of American studios from the 1880s-1920s, variegated in color, often of a milky, iridescent appearance.

Antique or Cathedral: Traditional glass of uniform and translucent color; the same as Pot Metal glass of medieval manufacture.

Slab (dalle de Verre): Pieces of glass, usually about one inch thick, often faceted, set within a concrete or epoxy resin matrix. A modern type of glass.

Jewels or Cast Glass: Nuggets of glass inserted into windows for a decorative effect.

Lead Came: Most common form of connecting individual pieces of glass. Usually of an "H" profile, the heart (or central bar) rests between the segments and the flanges (side bars) are pressed down to hold the glass in place.

Copper-foil: Thin strips of copper floated on solder often used to mend cracks.

Drapery: Opalescent type of glass formed into ridges to resemble drapery folds.

Plating: The use of one piece of glass on another of a different texture or color and leading them together for a special effect. Very often used in glass by Tiffany, La Farge, and other studios of the opalescent era.

Vitreous Paint: A mixture of finely ground glass, metallic oxides, and a liquid mixing agent use for painting on glass. It has to be fired for permanent adhesion.

Silver Stain: A nitrate applied to the exterior of glass, popular since the 14th century. When fired it produces a variety of yellow shades. Silver stain was used with great sophistication in English late medieval and 19th-century styles, especially in the canopy designs that frame figural images.

Enamels: Vitreous colors applied to glass. The enamel colors were developed in the Renaissance, used through the 18th century, and often found in the flesh areas of glass of 19th-century German and the Opalescent studios.

Etching or Sandblasting: Processes that alter the surface of the glass with acid or sand at high pressure; often a layer of another color glass is revealed. Often used in inscriptions.

SUBJECT MATTER

The subjects of window are sometimes difficult to recognize since often the users of a religious edifice have lost track of the meaning of some of the images. One can only make an effort and include a sufficient description of the window (Description of Subject) to help a reader. If the subject is known, include anything unusual about the window. For example, the Visitation window of St. Michael's Church, Providence, shows both husbands as well as Mary and Elizabeth participating in the Visitation scene. A handy paperback guide to symbolism often makes interpretation of subjects easier.

James Hall. Dictionary of Subjects and Symbols in Art. New York: Harper & Row; Icon Editions. Most recent and comprehensive.

George Ferguson. Signs and Symbols in Christian Art. New York: Oxford University Press.

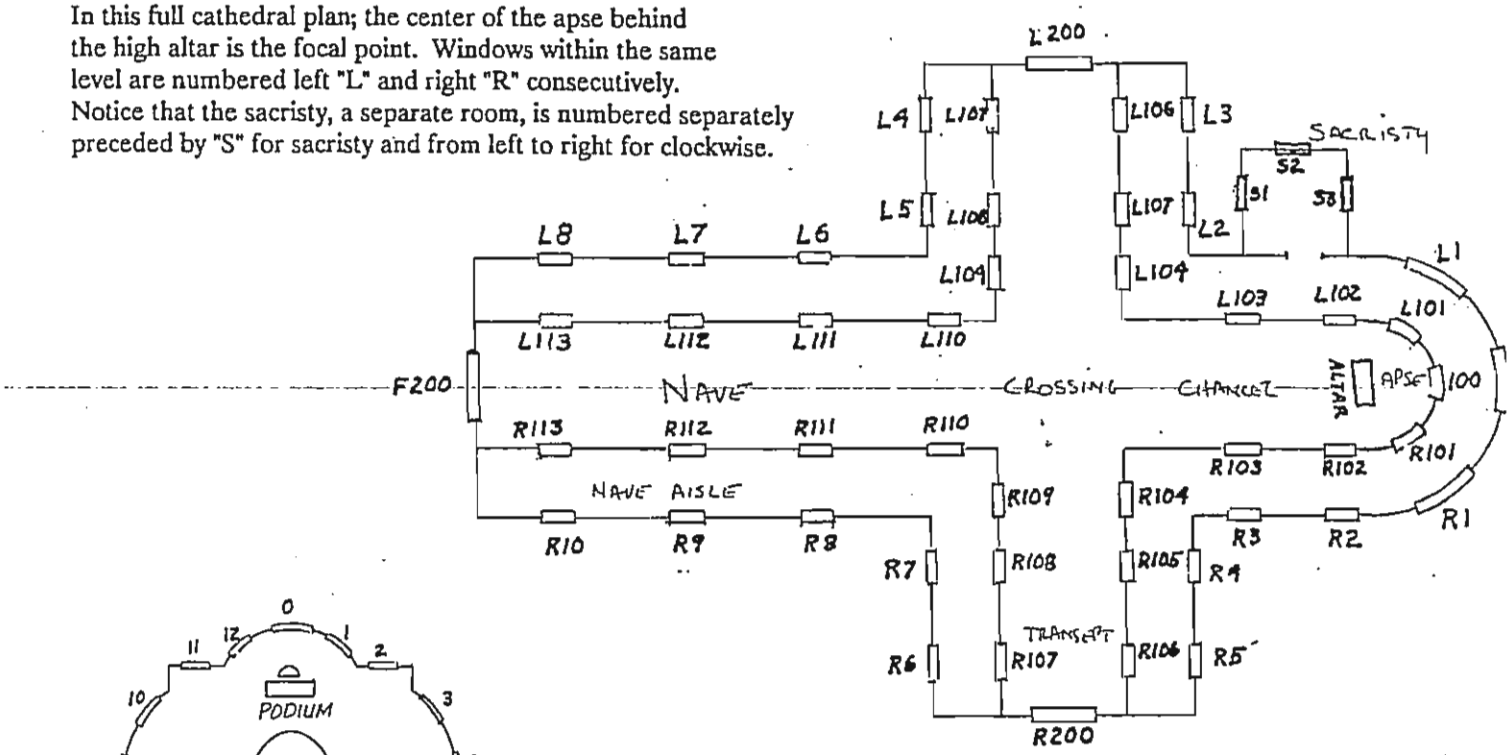
Emile Mâle. The Gothic Image. Princeton: Princeton University Press. Particularly for Gothic Revival programs.

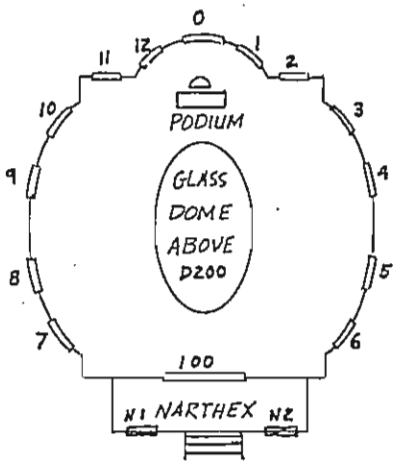
THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA
NUMBERING WINDOWS AND WINDOW SHAPES FOR SITELIST FORMS

Two numbering systems are suggested but both require that numbering begin at the focal point of the space (altar, ark, podium, judge's bench, etc). All windows are numbered whether or not they contain stained glass. Ground fl windows are numbered from 0 to 99; next level from 100 to 199 and so on. The two numbering systems ar : SYMMETRICAL SYSTEM and the CONSECUTIVE SYSTEM.

SYMMETRICAL SYSTEM

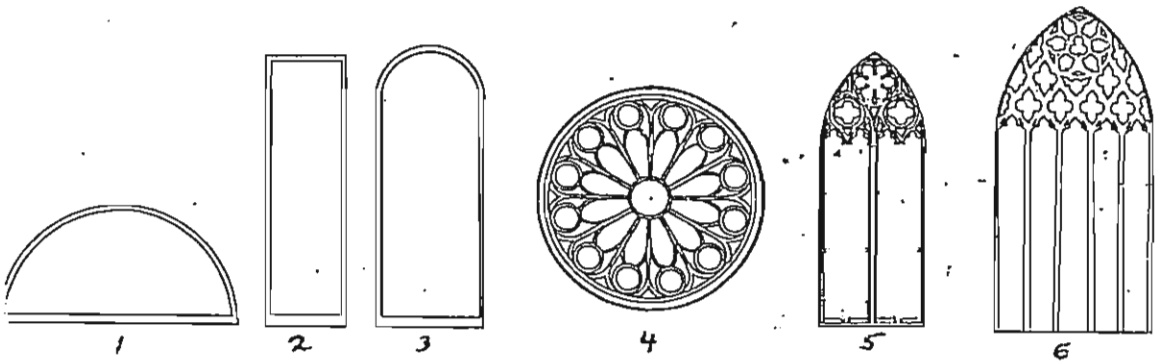
In this full cathedral plan; the center of the apse behind the high altar is the focal point. Windows within the same level are numbered left "L" and right "R" consecutively. Notice that the sacristy, a separate room, is numbered separately preceded by "S" for sacristy and from left to right for clockwise.





CONSECUTIVE SYSTEM

Example of a building with two levels of windows and a glass dome in the ceiling. The building is numbered consecutively and clockwise from the focal point behind the podium. The narthex is numbered separately and the dome on the third level is preceded by "D" for dome.



WINDOW SHAPES: Six general window shapes are presented. Select the shape that corresponds most closely to the window under study and enter the number on the line designated "Window Shape."

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA

SITELIST FORM

Researcher _____
Street _____
City _____
State & Zip _____ Phone _____

Date _____ Time expended _____
Slides?
Photos?

BUILDING SKETCH PLAN

State _____ County _____ City _____ Zip _____

Name of Building _____

Function or Type _____

Address _____

Contact Person, Title _____ Phone _____

Date of Construction _____ Architect _____

Alteration, Date _____ Architect _____

Number of Figural Windows _____ Ornamental Windows _____
(Including Scenic or Abstract)

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA

WINDOW DATA

Researcher

Date

Building

City

Location & Number on Plan _____ Window Shape: _____ Date of Window: _____
(If Ornamental, just group windows but give numbers)

Attributed to: _____ Signature _____

Subject of Window _____

Dimensions: H. _____ W. _____

Inscriptions _____

_____

_____

_____

Type of Glass and Technique (Check as many as apply)

Opalescent ___
Antique or Cathedral ___
Slab (dalle de Verre) ___
Jewels or Cast Glass ___
Other _____

Lead Came ___
Copper-foil ___
Drapery ___
Plating ___

Vitreous Paint ___
Silver Stain ___
Enamels ___
Etching or Sandblasting ___

Description of Subject (Brief) _____

_____

Arms (if applicable)

Donor _____ Memorial to: _____

Condition of Window _____

Exterior Protection _____

Restoration _____ Date _____

Bibliography _____

_____

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA

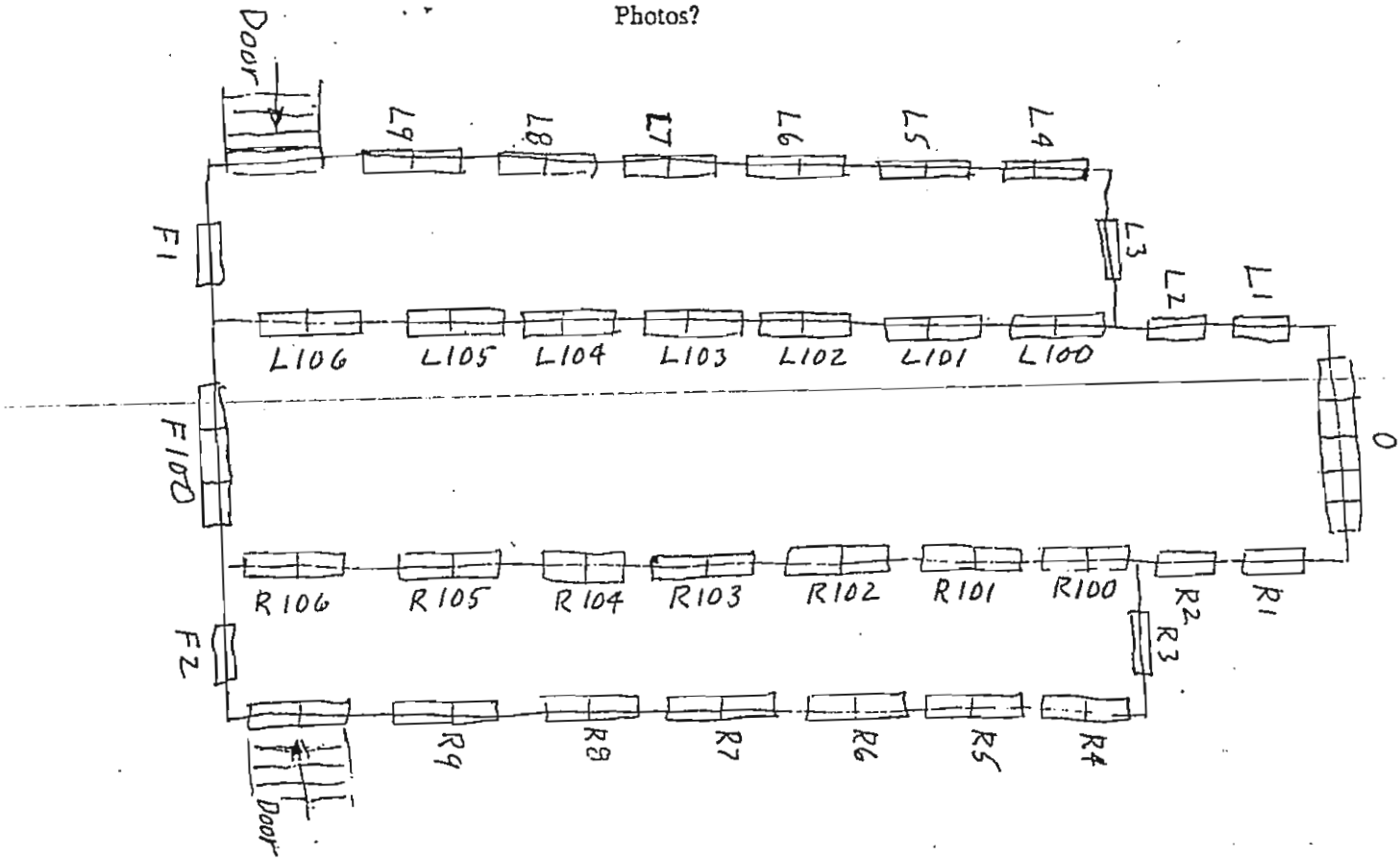
SAMPLE

SITELIST FORM

Researcher Hayward, Duhe, Voorsanger
Street Cloisters, Fort Tryon Park
City New York, N.Y.
State & Zip 10040 Phone (212) 923-3700

BUILDING SKETCH PLAN

Date 10/22/89 Time expended 4 hrs
Slides? ✓
Photos?



State RI County Newport City Newport Zip 02840

Name of Building St. Mary's Roman Catholic Church

Function or Type Parish

Address Spring Street

Contact Person, Title Father Daniel Gray Phone

Date of Construction 1848-1853 Architect Patrick C. Keeley, Brooklyn N

Alteration, Date 1892-95 and 1985-6 Architect Marchesi Co. N.Y. (protective glas

Number of Figural Windows 36 Ornamental Windows 0
(Including Scenic or Abstract)

THE CENSUS OF STAINED GLASS WINDOWS IN AMERICA

WINDOW DATA

SAMPLE

Researcher C H V

Date 10/22/89

Building St Mary's

City Newport

Location & Number on Plan Bay R6 Window Shape: 5 Date of Window: 1892-95
(If Ornamental, just group windows but give numbers)

Attributed to: Tiroler Glasmalerei, Innsbruck Signature Bill signed "L. Art Glass Co." Aus:

Subject of Window The Annunciation / God the father in Rose

Dimensions: H. 102" W. 24" each light Rose 36"

Inscriptions Donated by / Mrs. Theodore Havemeyer

Type of Glass and Technique (Check as many as apply)

Opalescent ___	Lead Came ✓	Vitreous Paint ✓
Antique or Cathedral ✓	Copper-foil ___	Silver Stain ✓
Slab (dalle de Verre) ___	Drapery ___	Enamels ✓
Jewels or Cast Glass ___	Plating ___	Etching or Sandblasting ✓
Other Flashed & abraded		

Description of Subject (Brief) Angel appears to Virgin interrupted at reading desk, Vase of lilies symbol of Virgin's purity. God dispatches Dove of the Holy Spirit in rose above.

Arms (if applicable)
None

Donor Mrs. Theodore Havemeyer Memorial to: none

Condition of Window good - One small piece missing at bottom & another in rose at top.

Exterior Protection yes - exterior glass in frames

Restoration Marchesi Co, N.Y. Date 1985-6

Bibliography Newspaper Clippings and bills in Church Office

The Census of Stained Glass Windows in America

Site Data

Contact/Researcher J. FARNSWORTH & TEAM Organization PHILA. HIST. PRES. CORP.
Address 1616 WALNUT STREET City PHILADELPHIA State PA Zip 19103
Phone: Day (215) 546-1146 Evening (215) 546-1146
Date of survey 1/7/92 Time expended 6 HRS, + RESEARCH

Present name of building ST. MARK'S EPISCOPAL CHURCH
Original name of building ST. MARK'S EPISCOPAL CHURCH
Function or type (if religious, include denomination) EPISCOPAL
Address 1625 LOCUST STREET
City PHILADELPHIA State PA Zip 19103 County PHILA.
Contact person and title GAIL BACHMAN, ADMIN. ASSIST. Phone (215) 555-1212

Year of construction 1848 - 1849 Architect JOHN NOTMAN
Alteration year 1900 Architect COPE & STEWARDSON
Number of figural windows 45 Number of ornamental windows 0
(Include scenic or abstract) (Standard catalogue patterns routinely reproduced)

Complete the building plan using the following key. If other abbreviations are needed, please indicate them on the key. A *North* directional arrow should be placed in the circle provided.

B = Baptistry	F = Facade	N = Narthex	SK = Skylight
CH = Chapel	H = Hall	R = Right	ST = Stair
D = Dome	L = Left	S = Sacristy	T = Tower

Window summary report THE MAJORITY OF WINDOWS ARE ENGLISH: THERE ARE TWENTY-FOUR BY LAVERS, BARRAUD & WESTLAKE, SEVEN BY CLAYTON AND BELL (THREE OF THESE IN THE CLOISTER, PREFIX CL), ONE BY BURLISON & GRYLLS, ONE BY JOHN HARDMAN, ONE BY C. BOOTH (HIS ENGLISH STUDIO?) AND SIX IN THE CHAPEL BY C. E. KEMPE. THERE IS A WINDOW CONSISTING OF A 16th C. SWISS PANEL THAT IS COMBINED WITH TWO 19th C. PANELS BY THE MAYER STUDIO WHICH MIMIC THE 16th C. PANEL, AS WELL AS TWO TYPICAL MAYER WINDOWS. THERE ARE TWO AMERICAN WINDOWS, ONE BY D'ASCENZO AND ONE BY DUNCAN NILES TERRY. VESTRY MINUTES RESEARCHED BY MARJORY ROTH.

The Census of Stained Glass Windows in America

Site Data

Contact/Researcher _____ Organization _____
Address _____ City _____ State ___ Zip _____
Phone: Day _____ Evening _____
Date of survey _____ Time expended _____

Present name of building _____
Original name of building _____
Function or type (if religious, include denomination) _____
Address _____
City _____ State _____ Zip _____ County _____
Contact person and title _____ Phone _____

Year of construction _____ Architect _____
Alteration year _____ Architect _____
Number of figural windows _____ Number of ornamental windows _____
(Include scenic or abstract) (Standard catalogue patterns routinely reproduced)

Complete the building plan using the following key. If other abbreviations are needed, please indicate them on the key. A *North* directional arrow should be placed in the circle provided.

B = Baptistry	F = Facade	N = Narthex	SK = Skylight
CH = Chapel	H = Hall	R = Right	ST = Stair
D = Dome	L = Left	S = Sacristy	T = Tower

Window summary report _____

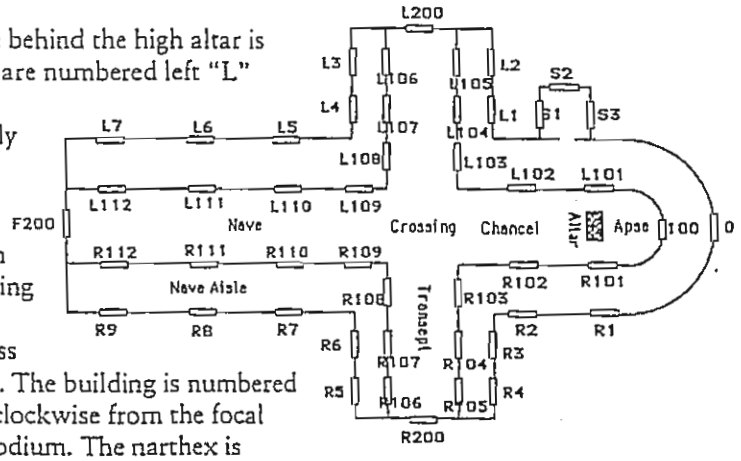
The Census of Stained Glass Windows in America

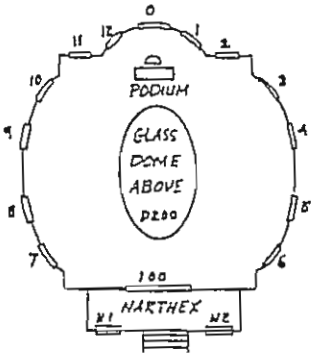
Numbering Windows and Window Shapes

Two numbering systems are suggested but both require that numbering begin at the focal point of the space (altar, ark, podium, judge's bench, etc.) All windows are numbered whether or not they contain stained glass. Ground floor windows are numbered from 0 to 99; next level from 100 to 199 and so on. The facade (F) is numbered left to right, while facing the focal point. Windows in ancillary spaces should be numbered clockwise beginning left of entry. The two numbering systems are the Symmetrical System and the Consecutive System. The symmetrical system is preferred.

Symmetrical System

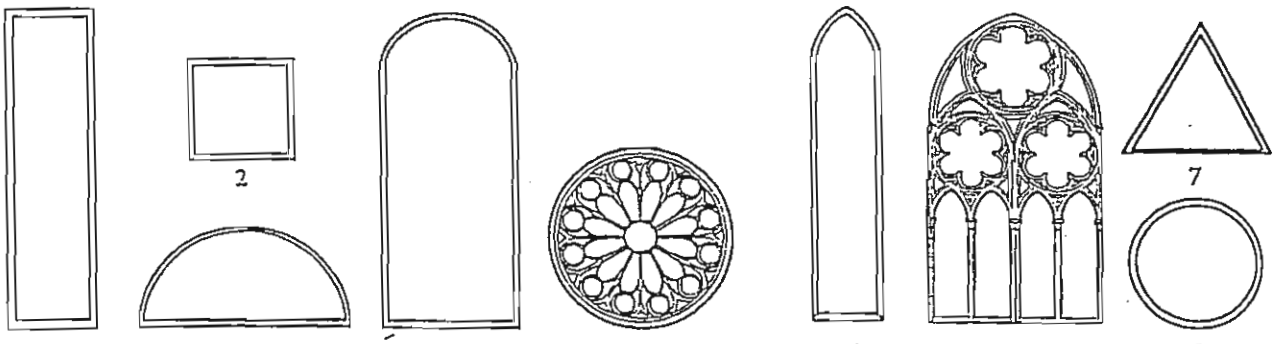
In this full cathedral plan, the center of the apse behind the high altar is the focal point. Windows within the same level are numbered left "L" and right "R" consecutively. Notice that the sacristy, a separate room, is numbered separately preceded by "S" for sacristy.





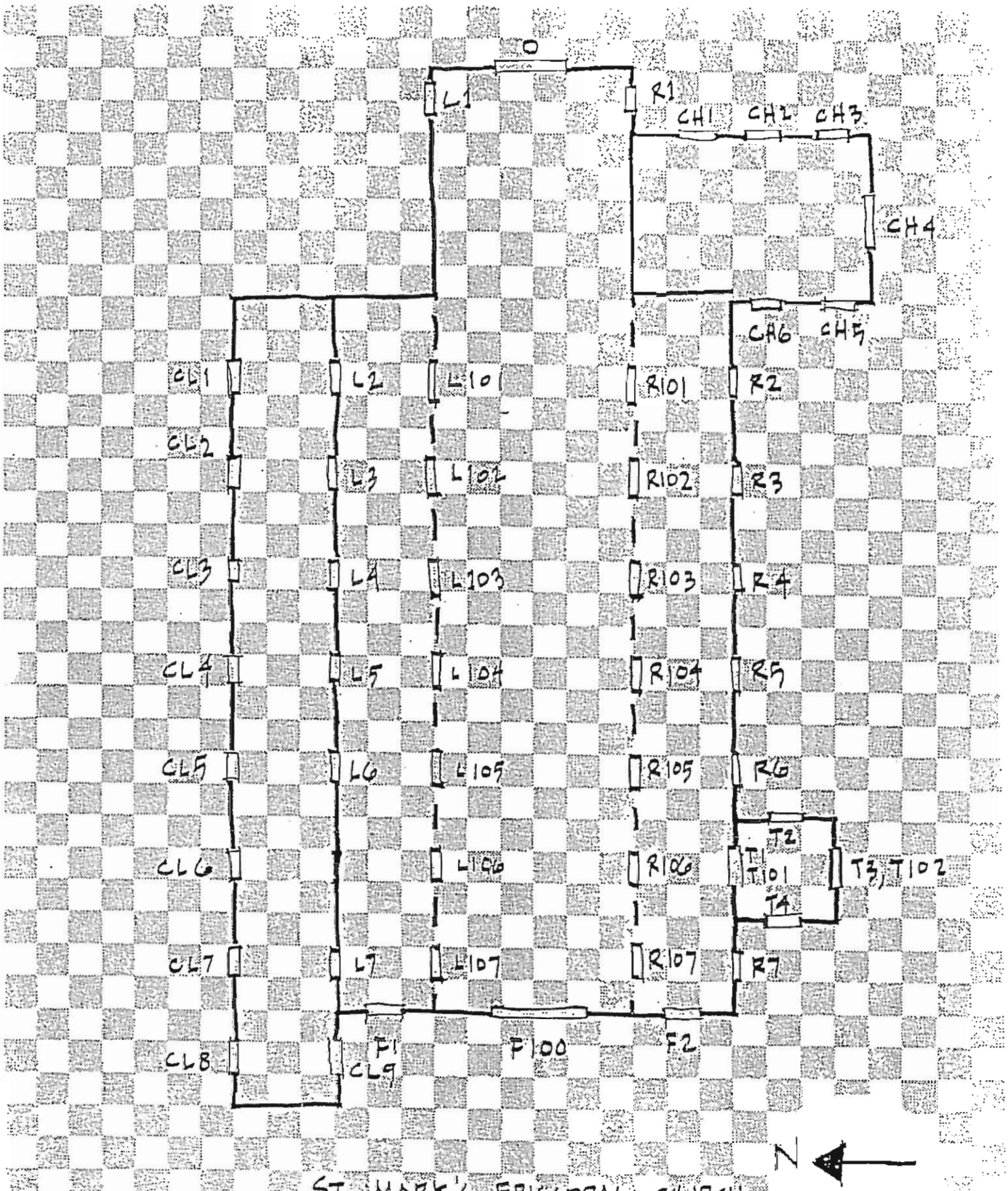
Consecutive System

Example of a building with two levels of windows and a glass dome in the ceiling. The building is numbered consecutively and clockwise from the focal point behind the podium. The narthex is numbered separately and the dome on the third level is preceded by "D" for dome.



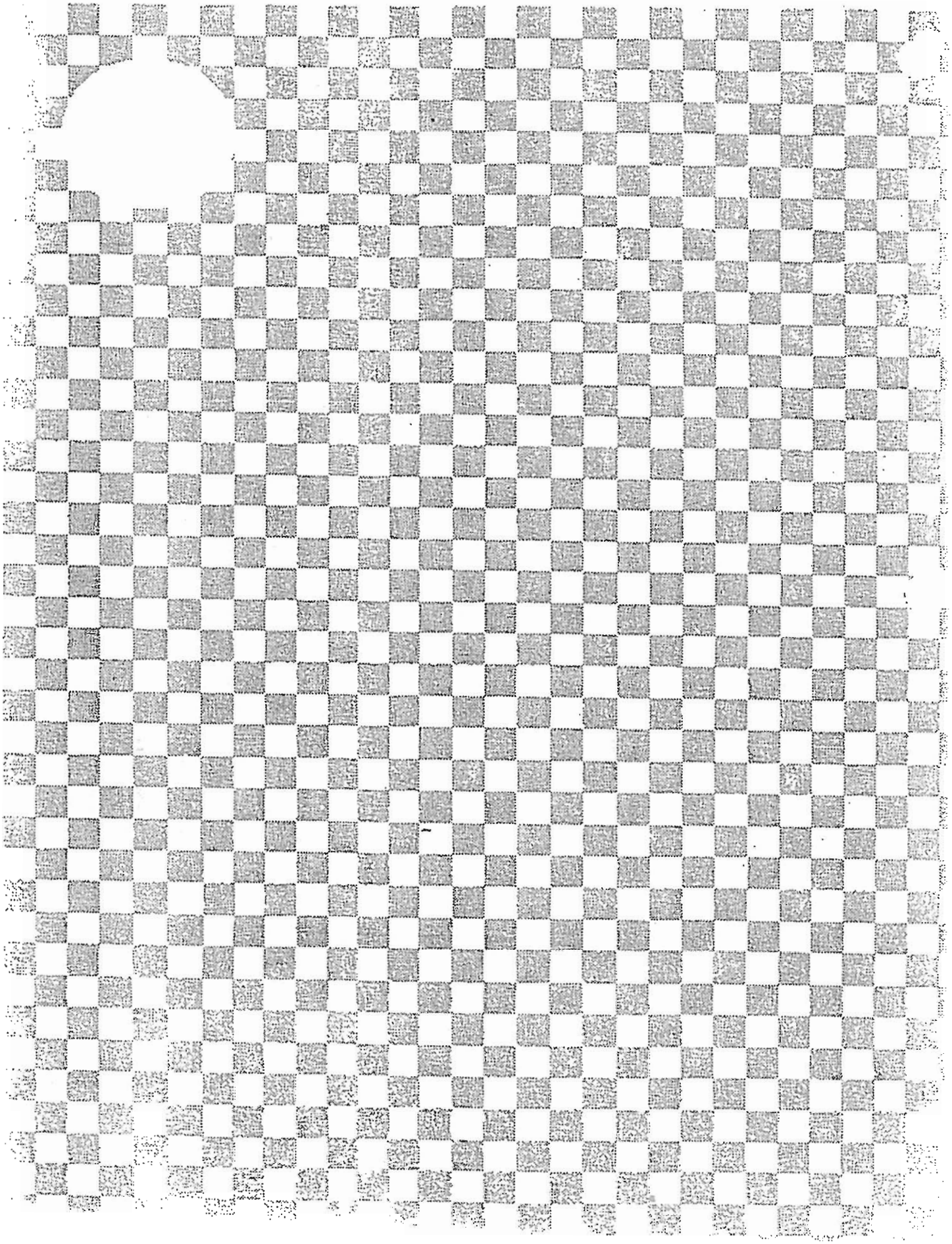
Window Shapes

Eight general window shapes are presented. You will find a variety of forms. For example, lancet windows (No. 6) may have a single light (6A) or multiple lights (6B). Two forms may be combined, such as Nos. 1 and 3. Select the shape(s) that corresponds most closely to the window under study and enter the number on the line designated "Window Shape."



ST. MARK'S EPISCOPAL CHURCH
1627 LOCUST ST.
PHILA., PA.

CL = CLOISTER



The Census of Stained Glass Windows in America

Surveyor C. JACOBS, M. STERN
Building ST. MARK'S EPISCOPAL CHURCH
Location and Number on plan R5
Dimensions:* HT 18 ft 16 in WD 4 ft 16 in
Shape CO Number of lights 2
Artist or studio LAVERS, BARRAUD & WESTLAKE
Signature LAVERS / BARRAUD / & / WESTLAKE / LONDON / 1878
Subject WISE AND FOOLISH VIRGINS
Inscriptions TO THE GLORY OF GOD / AND IN THE LOVING MEMORY OF JOSEPHINE VAN PELT MARCH 1870

Window Data

Local organization PHILA. HIST. PRES. CORP.
City PHILADELPHIA Survey date 1/7/92
Photo documentation ☑ yes ☐ no
Date 1878 ☑ Documented or ☐ Conjectured
Tracery ☑ yes ☐ no

Type of glass and technique (Check as many as apply.)

☐ Opalescent	☐ Flashed glass	☑ Lead came	☐ Enamels
☑ Antique or Cathedral	☐ Drapery	☐ Copper-foil	☑ Acid etching or sandblasting
☐ Slab (dalle de Verre)	☐ Machine textured	☑ Vitreous paint	☐ Other
☐ Plating	☐ Jewels or cast glass	☑ Silver stain	

Brief description of subject (and Coat of Arms if applicable) LEFT LANCET: LEFT, A SET OF STEPS LEADS THROUGH AN OPEN DOOR, UPWARDS, AND RAYS OF GOLDEN LIGHT RADIATE OUTWARD. FIVE WOMEN HOLD BURNING OIL LAMPS, ONE WOMAN LOOKS TOWARDS RIGHT LANCET. RIGHT LANCET: FIVE WOMEN HOLDING UNLIT LAMPS. ALL WOMEN ARE DRESSED IN ROBES EMBROIDERED IN GOLD, WITH CLOAKS OF CRIMSON, BLUE, GREEN AND DEEP GOLD. THE SURROUNDING FRAME IS ORNAMENTED W/ PLANT FORMS.

Donor UNKNOWN Memorial to JOSEPHINE VAN PELT
Condition: Matrix 1 Deflection 1 Glass 0 Paint 0 Dirt 1 Previous repair 0 *(0 = Excellent, 1 = Good, 2 = Fair, 3 = Poor)*
Frame: Wood ☐ Stone ☑ Metal ☐
Exterior protection: Leaded glass panels ☐ Laminated or tempered glass ☑ Wire ☐ Acrylic or polycarbonates ☐
Vented? ☐ yes ☑ no Restoration NOT EVIDENT Date —

Bibliography/Comments SIGNED AND DATED AS WELL AS LISTED IN PARISH REGISTER FOR 1878.

*Dimensions may be approximate.

The information on this form is limited to educational and scientific purposes. Any other use constitutes action totally independent of the CSGA and completely disassociated from its purposes. The CSGA and the above named organization assume no liability for the information contained herein and do not represent that said information is warranted to be correct and complete.

The Census of Stained Glass Windows in America

Surveyor _____

Building _____

Location and Number on plan _____

Dimensions:* HT ___ ft ___ in WD ___ ft ___ in

Shape _____ Number of lights _____

Artist or studio _____

Signature _____

Subject _____

Inscriptions _____

Window Data

Local organization _____

City _____ Survey date _____

Photo documentation ☐ yes ☐ no

Date _____ ☐ Documented or ☐ Conjectured

Tracery ☐ yes ☐ no

Type of glass and technique (Check as many as apply.)

☐ Opalescent	☐ Flashed glass	☐ Lead came	☐ Enamels
☐ Antique or Cathedral	☐ Drapery	☐ Copper-foil	☐ Acid etching or sandblasting
☐ Slab (dalle de Verre)	☐ Machine textured	☐ Vitreous paint	☐ Other _____
☐ Plating	☐ Jewels or cast glass	☐ Silver stain	

Brief description of subject (and Coat of Arms if applicable) _____

Donor _____ Memorial to _____

Condition: Matrix ___ Deflection ___ Glass ___ Paint ___ Dirt ___ Previous repair ___ *(0 = Excellent, 1 = Good, 2 = Fair, 3 = Poor)*

Frame: Wood ☐ Stone ☐ Metal ☐

Exterior protection: Leaded glass panels ☐ Laminated or tempered glass ☐ Wire ☐ Acrylic or polycarbonates ☐

Vented? ☐ yes ☐ no Restoration _____ Date _____

Bibliography/Comments _____

**Dimensions may be approximate.*

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Assessing the Condition of Stained Glass Windows

In assessing the condition of stained glass windows for a CSGA survey follow these guidelines and use the rating system 0-3, "UNK" if any portion is unknown, or "NA" if not applicable (especially for windows without paint).

Matrix: The matrix is the structure or material that directly holds and supports the glass. This can be one of, or a combination of, the following: lead came; zinc or brass came; copper-foil; epoxy or concrete; Babbit etal (Belcher-type windows). It also includes the tie wires, support bars and saddle bars. Inspect the matrix to determine the following: Is the matrix cracking? Is it corroding (evinced by white powder on surface of lead, zinc or copper-foil)? Is the matrix separating from the glass (are there light leaks between the glass edge and the matrix)? Are the support bars properly attached?

Use the scale:
0 = Excellent condition – No damage
1 = Good condition – Less than 1% of matrix affected
2 = Fair condition – 1% to 5% affected
3 = Poor condition – More than 5% affected

Deflection: Deflection is the bowing or bulging of the window away from its original design plane. It may be difficult to discern deflection of clerestory windows from the floor of the building. A good technique is to stand against the wall directly under the window and look up. Another technique is to study the lines of the design. The window is deflected if there are lines that appear curved that obviously should be straight.

Use the scale:
0 = Excellent condition – No deflection
1 = Good condition – Less than one inch of deflection
2 = Fair condition – One or two inches of deflection
3 = Poor condition – Greater than two inches of deflection

Glass: The individual pieces of glass held in the matrix. Inspect the glass for cracked pieces, missing pieces and/or unstable glass (evinced by internal fracturing or crazing).

Use the scale:
0 = Excellent condition – No damage
1 = Good condition – Less than 1% of glass affected
2 = Fair condition – 1% to 5% affected
3 = Poor condition – More than 5% affected

Paint: The applied surface decoration, excepting silver stain. This may consist of fired opaque or transparent vitreous paint (grisaille or enamel) or unfired paint i.e. oil or varnish. Inspect the paint for flaking, peeling and/or "faded" trace lines or non-existent mattes. (Glass paint cannot fade. What appears to be fading is the granular loss of paint.)

Use the scale:
0 = Excellent condition – No damage
1 = Good condition – Less than 1% of glass affected
2 = Fair condition – 1% to 5% affected
3 = Poor condition – 5% or more affected
Indicate not applicable, "NA" on unpainted windows

Dirt: Dirt collects on both surfaces of the glass and in between the plates on a plated window. The dirt detracts from the appearance of the window and creates an environment that encourages deterioration of the glass and matrix.

Use the scale:
0 = Excellent condition – Clean
1 = Good condition – Less than 1% of glass affected
2 = Fair condition – 1% to 5% affected
3 = Poor condition – 5% or more affected

Previous repair: Poor previous repairs can be divided into two categories: reversible and irreversible. Inspect the window for prior reversible repairs such as: lead flanges or dutchmen; application of additional support bars; recementing in place; and surface application of silicone. Inspect the window for irreversible repairs such as: new painted pieces; replacement of original glass; installation of aluminum frames or ventilators (which may obscure original design or signatures); or releading.

0 = Excellent – No previous repairs are evident
1 = Good – Reversible repairs, less than 1% of glass affected
2 = Fair – Reversible repairs, less than 5% of glass affected
3 = Poor – Any irreversible repairs

A window rating for The CSGA window data form is only a general indication of the condition of the window and is not meant to be a report for restoration guidelines. However, building owners may ask questions about methods of repair, and it is helpful to provide them with a copy of *Conservation and Restoration of Stained Glass: An Owner's Guide*, or information on how this booklet can be obtained. (See p. 60.)

DESCRIBING COLORED GLASS

There are 10 examples of early American glass. Describe each color first using ordinary visual assessment, then using the *Munsell Book of Color (Glossy)*. We can check amongst ourselves to see how consistent each type of assessment is from person to person. Notice how much each assessment changes when you change lighting conditions (e.g., daylight near window, fluorescent light).

Specimen #	Visual description	Munsell
example	*Deep reddish-brown (cranberry)*	*7.5R 3/12*
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		

The Munsell Color-Order System

The Munsell color-order system is a way of precisely specifying colors and showing the relationships among colors. Every color has three qualities or attributes: hue, value and chroma. Professor A.H. Munsell established numerical scales with visually uniform steps for each of these attributes. *The Munsell Book of Color* displays a collection of colored chips arranged according to these scales. Each chip is identified numerically using these scales. The color of any surface can be identified by comparing it to the chips, under proper illumination and viewing conditions. The color is then identified by its hue, value and chroma. These attributes are given the symbols H, V, and C and are written in the form H V/C, whic is called the "Munsell notation."

Hue

Hue is that attribute of a color by which we distinguish red from green, blue from yellow, etc. There is a natural order of hues: red, yellow, green, blue, purple. One can mix paints of adjacent colors in this series and obtain a continuous variation from one to the other. For example, red and yellow may be mixed in any proportion to obtain all the hues from red through orange to yellow. The same may be said of yellow and green, green and blue, blue and purple, and purple an red. This series returns to the starting point, so it can be arranged around a circle. Munsell called red, yellow, green, blue and purple "principal hues" and placed them at equal intervals around a circle. He inserted five intermediate hues: yellow-red, green-yellow, blue-green, purple-blue and red-purple, making ten hues in all. For simplicity, he used the initic as symbols to designate the ten hue sectors: R, YR, Y, GY, G, BG, B, PB, P and RP. The hue circle is illustrated on the chart labeled Munsell's Three Attributes of Color, found in the back pocket of this binder.

Munsell arbitrarily divided the hue circle into 100 steps, of equal visual change in hue, with the zero point at the beginning of the red sector, as shown in Figure 1. Hue may be identified by the number from 0 to 100, as shown in the outer circle. This may be useful for statistical records, cataloging and computer programming. However, the meaning is more obvious if the hue is identified by the hue sector and the step, on a scale of ten, within that sector. For example, the hue in the middle of the red sector is called "five red," and is written "5R." (The zero step is not used, so there is a 10R hue, but no 0 YR.) This method of identifying hue is shown on the inner circle.

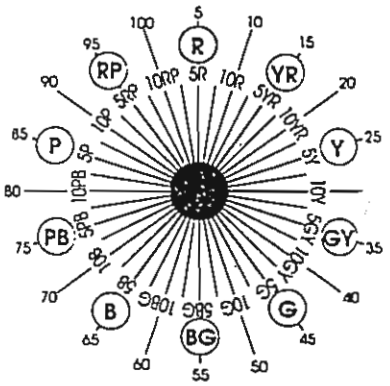


Figure 1: **Munsell Hue Designations**

The Primary Hue Circle

In 1993, Cal McCamy proposed a series of hue names for the hue circle, using the additive primaries – red, green and blue; the subtractive primaries – yellow, magenta and cyan; and four intermediate hues. The names are applied to the same set of hue sectors as the Munsell hues. This proposal corrects a well-known displacement of blue on the Munsell h circle, and it accommodates the thinking of the large number of people who work with color photography, color printing, color television, color copying and color computer monitors – technologies based on the additive and subtractive primaries. The correspondence between the Munsell hue circle and the primary hue circle is given in Table 1. Blue is the only instance where the same name has a different meaning (resulting from the deliberate use of that name for a different sector). In this case, the new word and symbol are distinguished from the old, when necessary, by the prime mark (Blue' and B').

The addition of this set of hue names does not involve any changes whatsoever to the colors in *The Munsell Book of Color* or any Munsell color standards. It is merely an alternate way of designating the same hues, for use in those fields in which it is found useful.

Table 1: **Correspondence Between the Munsell Hue Circle and the Primary Hue Circle**

Munsell Hue Circle		Primary Hue Circle	
Hue	*Symbol*	*Hue*	*Symb*
Red	R	Red	R
Yellow-Red	YR	Yellow-Red	YR
Yellow	Y	Yellow	Y
Green-Yellow	GY	Green-Yellow	GY
Green	G	Green	G
Blue-Green	BG	Cyan	C
Blue	B	Blue-Cyan	BC
Purple-Blue	PB	Blue'	B'
Purple	P	Magenta-Blue	
Red-Purple	RP	Magenta	M

▾alue

Value indicates the lightness of a color. The scale of value ranges from 0 for pure black to 10 for pure white. Black, white and the grays between them are called "neutral colors." They have no hue. Colors that have a hue are called "chromatic colors." The value scale applies to chromatic as well as neutral colors. The value scale is illustrated for a serie: of neutral colors on the chart labeled Munsell's Three Attributes of Color, found in the back pocket of this binder.

Chroma

Chroma is the degree of departure of a color from the neutral color of the same value. Colors of low chroma are sometimes called "weak," while those of high chroma are said to be "highly saturated," "strong," or "vivid." Imagine mixing a vivid red paint, a little at a time, with a gray paint of the same value. If you started with gray and gradually added red until the vivid red color was obtained, the series of gradually changing colors would exhibit increasing chroma. The scaling of chroma is intended to be visually uniform and is very nearly so. The units are arbitrary. The scale starts at zero, for neutral colors, but there is no arbitrary end to the scale. As new pigments have become available, Munsell color chip of higher chroma have been made for many hues and values. The chroma scale for normal reflecting materials extends beyond 20 in some cases. Fluorescent materials may have chromas as high as 30. A scale of chroma is illustrated on the chart labeled Munsell's Three Attributes of Color, found in the back pocket of this binder.

Munsell Notation

The complete Munsell notation for a chromatic color is written symbolically: H V/C. For a vivid red having a hue of 5R, a value of 6 and a chroma of 14, the complete notation is 5R 6/14. When a finer division is needed for any of the attributes decimals are used. For example, 5.3R 6.1/14.4. When the hues of the primary hue circle are used, the notation is written ir the same way, for example 2B' 5/4.

ɜ notation for a neutral color is written: N V/. (The chroma of a neutral color is zero, but it is customary to omit the zero i the notation.) The notation N 1/ denotes a black, a very dark neutral, while N 9/ denotes a white, a very light neutral. The notation for a middle gray is N 5/.

Munsell Color Space

Munsell hue, value and chroma can be varied independently so all colors can be arranged according to the three attributes in a three-dimensional space. The neutral colors are placed along a vertical line, called the "neutral axis" with black at the bottom, white at the top and all grays in between. The different hues are displayed at various angles around the neutral axis. The chroma scale is perpendicular to the axis, increasing outward. This three-dimensional arrangement of colors is called the "Munsell color space." The relationship of the three scales in three-dimensional space is illustrated on the chart labeled Munsell Color Space, which can be found in the back pocket of this binder.

Munsell Color Solid

All colors lie within a specific region of Munsell color space called the "Munsell color solid." Hue is limited to one turn around the circle. The scale of value is limited on the lower end by pure black, which is as dark as a color can be, and on the top by pure white, which is as light as a color can be. For a given value, there is a limit to the chroma that is possible, even with theoretically ideal coloring agents. Real coloring agents, with less than ideal characteristics, impose further limitations on physical representations of the color solid. The Munsell color-order system itself is applicable to all possible colors. The highest chroma yellow ɔlors have rather high values, while the highest chroma blue colors have lower ,lues. Thus the Munsell color solid has the irregular shape shown in Figure 2.

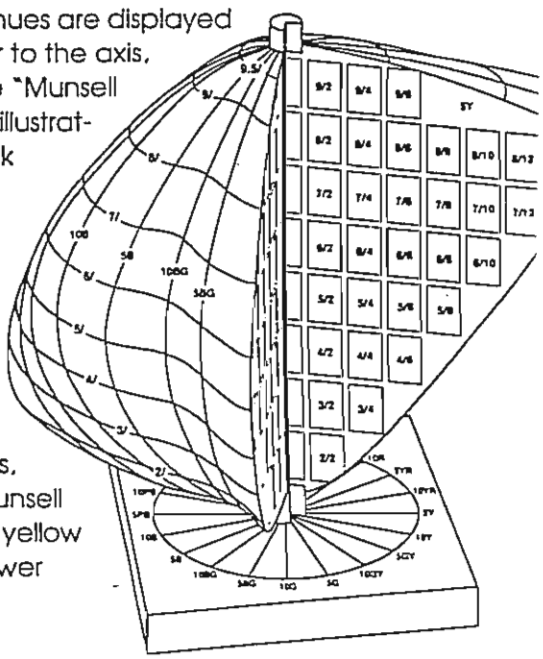


Figure 2: Munsell Color Solid

The Munsell® Book of Color, Glossy Collection

The Glossy Collection of *The Munsell Book of Color* displays nearly 1600 color chips, arranged according to the Munsell color-order system. Each page represents one hue, and there are 40 pages, 2.5 hue steps apart, in two volumes. The chips may be removed from the page to facilitate color comparison. On each page, the chips are arranged by Munsell value and chroma. Value increases from the bottom of the page to the top in increments of 1, while chroma increases outward from left to right in increments of 2. The Munsell hue is printed at the top of each page. The value steps are printed on a vertical scale on the left side of the page, and the chroma steps are printed along the horizontal scale at the bottom of the page. The standard way to write the description of a color using Munsell notations is to write the alpha-numeric designation for the Munsell hue (H) and the numeric designations for value (V), and chroma (C) in the form of H V/C.

For low-chroma colors, those that are nearly neutral (gray), small differences in chroma are readily apparent, while hue differences are less apparent. For this reason, colors with a chroma of 1 have been created for only 20 hues in the collection. These 1-chroma colors can be found at the back of each volume on the pages labeled Munsell Grays.

At high chromas, hue differences between adjacent hues in the book appear larger. Therefore it is desirable to have colors between those steps. Wherever achievable, colors have been produced for the hues midway between the 40 hue pages, for chromas of 12 and higher. These 78 supplementary colors can be found at the back of each volume on the pages labeled Munsell Supplementary Colors.

The gamut of colors in the Glossy Collection is limited by the physical properties of the materials used to make the chips. These limits encompass the colors of almost all natural and man-made materials. The darkest colors have a value of 2, and the lightest have a value of 9. High-chroma yellows are lighter than high-chroma colors of other hues, so for these colors, a special series of colors of value 8.5 is displayed.

A closely spaced scale of value called the Munsell Neutral Value Scale is displayed by a special series of neutral colors (black, white and grays). It has 37 colors ranging from a Munsell value of 0.5 (black) to a value of 9.5 (white), in steps of 0.25. The Munsell Neutral Value Scale is found in the back pocket of Volume 1 of this collection.

GLASS AND STAINED GLASS WORKSHOP
Loss Compensation on Three-Dimensional Glass

Deborah Long, July, 1998

I. Object Preparation

A. Repair: where possible, make all structural repairs to the object prior to loss compensation.

B. Cleaning: clean the glass with acetone, including edges of the loss area. It's a good idea to clean the whole surface to minimize the potential for later problems. Be sure to remove stray bits of cured epoxy and every bit of tape residue.

C. Note: these materials and techniques are only suitable for use on chemically stable glass . Repairs to deteriorated, weathered, or unstable glass should only be carried out by or under the supervision of experienced conservators.

II. Mold Making Materials

A. Silicone Rubbers: manufactured by several companies; examples below represent personal preferences and are chemically compatible with each other.

1. Dow Corning RTV 3110®: tin cure system (see product literature in notebook); two different catalysts: twenty-four hours, and four minutes. Very low shrinkage, moderate tear strength, accommodates moderate undercuts, excellent detail reproduction.

2. Dow Corning HSII®: tin cure system (see product literature in notebook); several catalysts useful for a variety of applications. Very flexible, high tear strength, almost no shrinkage, accommodates deep undercuts, excellent detail reproduction. This system includes a thixotropic additive, allowing molds to be made on vertical surfaces.

B. Wax: sheet type dental waxes come in several levels of hardness and many brands; useful for simple shapes only; care is required in use because molds are easily deformed by handling.

C. Tape: heavy polyester carrier, with acrylic adhesive; can be used on small flat sections of glass or along jagged break edges with losses; used primarily as a backing.

III. Fill Materials:

A. Epoxies: two part systems (see product literature in notebook) examples: Hxtal NYL®, Epotek 301-2®, Epotek 301®.

1. advantages: low viscosities, low shrinkage; long cure time allows release of trapped air; good level of transparency; very hard; strong bond to glass.

2. disadvantages: cure time at room temperature for Hxtal NYL is more than a week; limited long term stability: Hxtal 5-20 years, Epoteks 5-15 years; stability very dependent on careful measuring of resin and catalyst; sometimes unpredictable results when colored; limited number of epoxies available that meet the requirements of conservators; limited matches to index of refraction range of glass.

B. Polyester Resins: two part systems; examples: Castolite®, Akemi® brands

1. advantages: short cure time (usually less than an hour), easily colored

2. disadvantages: exothermic cure; shrink during cure, poor long-term stability, discoloring within one to two years (and sometimes less).

C. Colorants:

1. dyes: Orosol® dyes from Ciba Specialty Chemicals can be

ground with previously mixed resin and catalyst; produce transparent colors; however, dyes fade in a relatively short amount of time; they are somewhat unstable when mixed with epoxy (sometimes they look great when poured in the mold, but change colors as the resin cures).

2. pigments: dry pigments can be ground with previously mixed resin and catalyst. Pigments have a tendency to settle out during cure, leading to uneven distribution of color; particles must be very finely ground to avoid a "grainy" appearance; Ciba Specialty Chemicals produces a line of encapsulated micro particle pigments called Microlith WA® series. The particles are dispersed in an acrylic vehicle generally compatible with epoxy systems.

IV. Mold Making Procedures:

A. Choose the correct location: wherever possible choose another part of the object with the same profile and conformation. It is also important to make a mold big enough to have some "keying points" if possible.

B. Provide a release agent: apply a very thin coat of microcrystalline paste wax to the area to be molded. Using a soft cotton cloth, buff the wax immediately and thoroughly. Any waxy streaks left on the surface will be duplicated in the mold.

C. Choose the correct mold making material:

1. If the shape of the area to be molded is a relatively small and simple one, mix some fumed silica or glass micro-balloons (wearing a dust mask) with the 3110 RTV silicone rubber to thicken it. Add the number 4 catalyst at the recommended rate of 100:1 by weight and mix thoroughly but quickly. This catalyst causes the resin to set in approximately four minutes, so work fast! Apply the resin to the area to be reproduced and allow it to cure.

2. If the shape is more complicated, mix the HSII with one of it's several catalysts at the appropriate ratio. Paint a thin layer over the area to be molded. Then add 3-5% by weight of thixotropic additive, mix, and apply over the thin layer. Allow it to cure

3. If the shape is very simple, warm a sheet of wax slightly with a heat gun and press it to the glass. Apply more heat and finger pressure as needed, to bring the wax sheet into conformity with the shape of the object. Allow the wax to cool completely.

V. Casting Procedures

A. Prepare the mold for casting: after the appropriate amount of cure time has elapsed, carefully remove the mold from the glass. Remove the wax release agent from the glass. Trim the mold to a manageable size and test fit it to the loss. Choose a good orientation for the object and mark the high point on the mold. Cut a small hole at this point and, depending on the size of the loss, insert two tubes just shy of the inner surface of the mold. Seal them to the mold with a small amount of silicone rubber. For wax molds, you can sometimes use two sheets of wax and leave the top open for filling.

B. Apply the mold to the loss: place the mold on the loss area, keying it to the surrounding areas (where possible). Adhere it with more silicone rubber, making sure to press the mold firmly against the glass for a good seal. Wax molds can be attached to the glass by running a heated spatula along the edge of the mold to melt it in place.

C. Fill the mold: measure and mix the resin carefully, avoiding the introduction of air bubbles; and add colorants if necessary. Fill the mold with a glass pipette or syringe slowly, allowing the resin to flow into the mold and push air ahead of it. Fill until the resin reaches the tops of the tubes, providing a reservoir to fill any unseen voids. Allow the resin to cure.

VI. Finishing Procedures

A. Remove the mold: peel the mold from the object. You should be looking at a beautiful fill, perfect in color, clear, and inconspicuous (this seldom happens!).

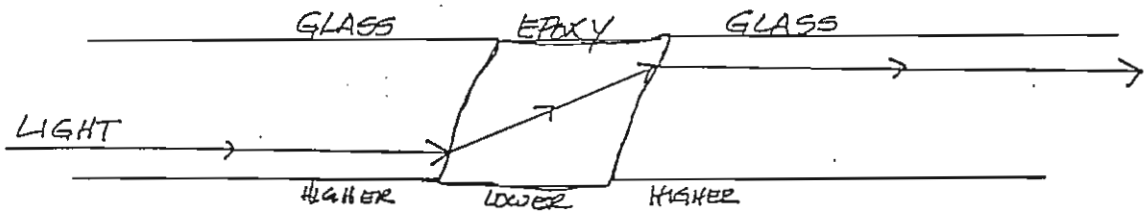
B. Clean up the fill: if your fill is not perfect, a new scalpel blade can be used to carve away excess material. Voids will have to be filled with more resin.

C. Polish: carved areas need to be rubbed down with successively finer grades of abrasive cloth, such as Micromesh®. To avoid damage to the surrounding glass, isolate it with tape or B-72. After working through all the grades, there will still be a fine haze. This might be acceptable, depending on the appearance of the object.

D. Apply a top coat: if the surface must be clear, apply a thin layer of B-72 or fresh epoxy to a thoroughly cleaned surface. It is also possible to polish the fill with a felt or muslin buff on a flex shaft handpiece or by hand with proprietary polishing compounds, although epoxy fills are easily melted by the high speeds of buffing equipment.

THE INDEX OF REFRACTION
AND
THE REPAIR AND FILLING OF GLASS

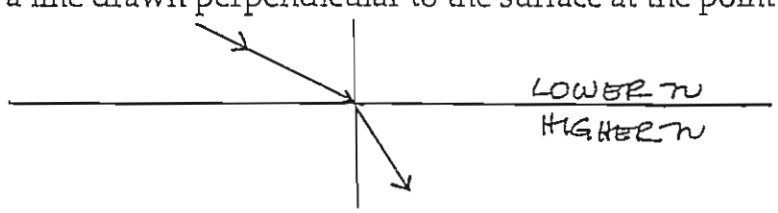
The index of refraction for a piece of glass is a measure of the amount that a light wave is bent upon passing from the air or another medium (a liquid, or a solid) into the piece of glass. In the case of glass repair, it can be used as a measure of the amount a light wave is bent when it passes from the original glass into the repair glue line and then back into the adjacent glass.



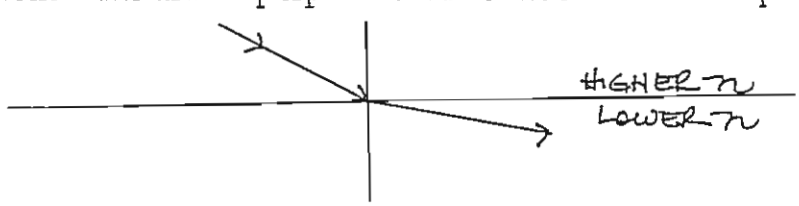
The Index of Refraction (n) is a pure number that is the ratio of the velocity of light in a vacuum (v) to its velocity in the medium in question (V).

$$n = v / V$$

When light passes from a medium of one n into a medium with a higher n, it will be bent toward a line drawn perpendicular to the surface at the point of entry.



When light passes from a medium of one n into a medium with a lower n, it will be bent away from a line drawn perpendicular to the surface at the point of entry.



Therefore, when a colorless substance is placed in a medium that has the same n, the substance will appear invisible. Early methods to measure the index of refraction for a crystal (or, in our case, a chip of glass) involved immersing the sample in liquids if differing n until the sample became invisible. Mineral fragments and glass fragments are usually thicker in the center than around the edges. This variation in thickness allows the particles to act as crude lenses, converging or dispersing light that passes through the particle. If the surrounding liquid is of a lower n, the particle will act as a converging lens,

concentrating light within the particle. If the surrounding liquid is of a higher n, the particle will act as a diverging lens and light will diverge from the particle.

If the difference between the two n is slight, the converging or diverging light rays will appear as a thin bright line near the interface of the two materials called the Becke line. As the microscope tube is raised, or as the stage is lowered, the Becke line will move toward the medium of higher index of refraction. Use of the Becke line allows one to use a series of liquids of known index of refraction to accurately and quickly estimate the index of refraction of a glass chip or mineral sample.

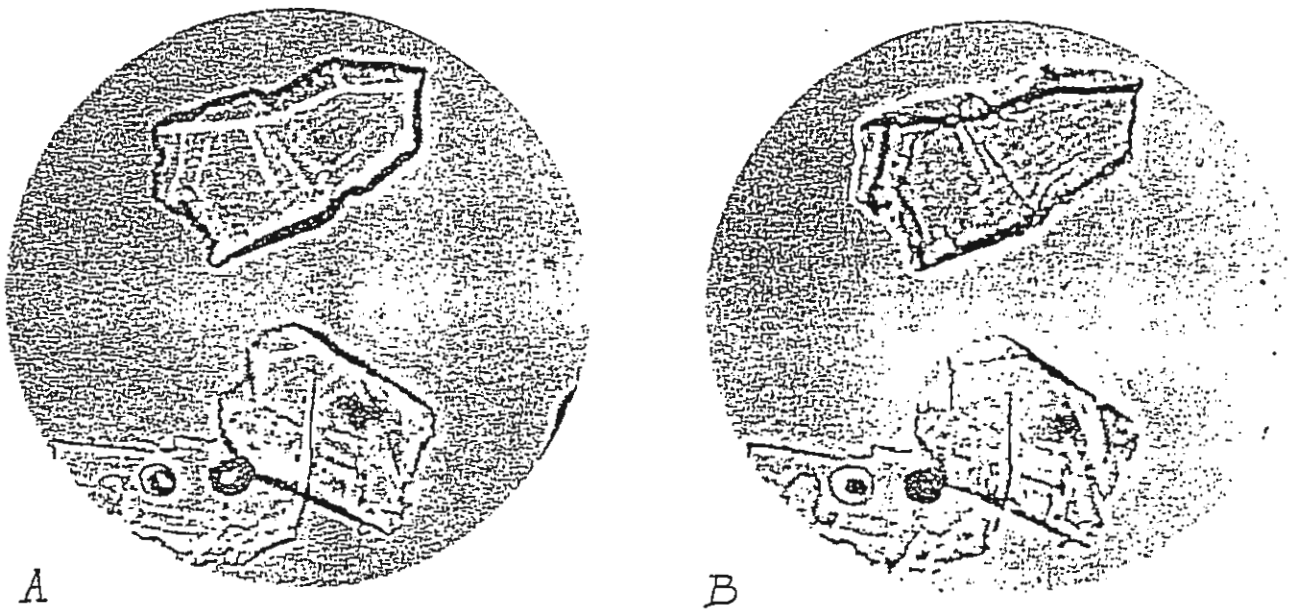


FIGURE 3-2. The Becke line. (A) When the refractive index of the fragment is *greater than* that of the immersion medium, the Becke line will move into the grain as the microscope tube is raised (or as the stage is lowered). (B) When the refractive index of the fragment is *less than* that of the immersion medium, the Becke line will move into the immersion oil as the tube is raised (or stage lowered).

Material for this handout is primarily paraphrased from the following text:
Phillips, W. R. 1971, *Mineral Optics: Principles and Techniques*. San Francisco: W. H. Freeman and Company.
Sketches are by J. Reilly.
Prepared for the Conservation and Restoration of Glass and Stained Glass Workshop, Ford Center, July, 1998.
Refractive Index Liquids used:
Cargille *Certified* Refractive Index Liquids, Series RF, Cat: 18005, Set: RF 1/5.

Glass and Stained Glass Conservation Workshop

SOME RESINS USED IN CERAMIC AND GLASS REPAIR

CLASS	NAME/ADDRESS	RI	Tg	APPEARANCE	SET-TIME	VISCOSITY	NOTES
EPOXIES	HXTAL NYL-1 Conservator's Emporium 100 Standing Rock Circle Reno, NV 89511	1.520		clear, "non-yellowing"	7days at 77° F Pot life - 2 hrs 2 days @ 95° F	Low	use a lamp to speed setting - or heat to 100 F - low shrinkage Mixing Ration: A:B = 3:1 by weight Yellows over time
	Hxtal Crystal Plus			clearer than hxtal nyl	8 days at room temp		May be hard to find
	Ablebond 342-1 Able Stik Laboratories 833 W 182nd Street Gardenia, CA 90248	1.564		clear	48 hours above 75°F Pot life - 8 hours No longer available	low 2000 cps	warm if crystallizes - heat slightly before applying No longer available
	Araldite AY 103 (HY 951) Ciba/Geigy Plastics & Additives Co. Plastic Division Duxford, Cambridge CB2 40A UK	1.574 - 1.578		clear - slightly yellow	36 hours at 68°-77°F Pot life - 3 hours	low 700-1100 cps	yellows - no longer available
	Epotek 301 Epoxy Technology Inc. 65 Grove Street Watertown, MA 02172	1.538-1.540	48°c	clear - slightly yellow	12 hours @ room temp 1 hour at 65° C Pot life - 45 min	low 100 cps	yellows on aging; surface sometimes remains slightly tacky when pulled from mold
	Epotek 301-2	1.564	65°c	clear	48 hours @ room temp 1 - 5 hrs @ 80°c Pot life 8 hrs	300-600 cps	

SOME RESINS USED IN CERAMIC AND GLASS REPAIR

CLASS	NAME/ADDRESS	RI	Tg	APPEARANCE	SET-TIME	VISCOSITY	NOTES
CYANOACRYLATES	Eastman 910 Eastman Chemical Prod. Inc. Chemical Division Kingport, TN 37662	1.450		clear	20-30 sec	very low 60-100 cps	turns white on settling - yellows - acetone is solvent
	Aron Alpha Toagosei Chemical Co. Ltd. Tokyo Japan (Conservation Materials)			clear	20-60 sec maximum strength after 12 hours		acetone is solvent - yellows (also see Loctite Super Glue)
POLYESTER RESINS	Akemi Wood & Stone, Inc. 5920 Old Saw Mill Road Fairfax, VA 22030	1.549-1.565		available in buff, white & transparent flowing, buff knife grade, trans. Knifegrade, limestone super (buff)	15-20 min @ room temp	varies w/type	very strong - yellows - slightly purple on setting
	Technovit 4000 Rupert & Co., Ltd. Dennings, Road Cheadle, Cheshire			transparent - slight green tint	10-15 min @72° F working time 5 - 7 min		exothermic - batches should not exceed 30g - green on setting
	Tiranti Clear Embedding Resin A. Tiranati Ltd. 21 Goodge Place London W1	1.549-1.565					
	Castolite Resin Buehler 41 Waukegan Road Lake Bluff, IL 60044	1.55		transparent	6-8 hrs Pot life - 45 min	320-340 cps	allow to gel @ room temp

SOME RESINS USED IN CERAMIC AND GLASS REPAIR

CLASS	NAME/ADDRESS	RI	Tg	APPEARANCE	SET-TIME	VISCOSITY	NOTES
ACRYLICS	Acryloids Rohm & Haas Independence Mall West Philadelphia, PA 19105 B-72, B48N, B-67, others	1.475-1.502	varies	clear	varies	varies	see compiled product liturature
	Rhoplex Acrylic Emulsions Rohm & Haas Independence Mall West Philadelphia, PA 19105 AC33, N580, AC73, AC234	1.475-1.502	varies	clear	varies	varies	see compiled product literature also see acrylic dispersions
MISCELLANEOUS	Cellulose Nitrates eg: Duco Cement, HMG UHV, Durafix)	1.497-1.512		yellow	varies	varies	contain stabilizers-check product literature
	U. V. Curing Adhesives (eg: Opticon UV-57 P. O. BOX 2445 Palos Verdes Peninsula, CA 90274 and others)	1.531	-	clear	depends on exposure to UV light	low	currently being studied as a option - object must be clamped in place for UV exposure (results seem variable)
POLYVINYL ACETATES	AYA Series (Union Carbide) Sold by Conservation Support System P. O. Box 91746 Santa Barbara, CA 93190	1.455-1.470	varies with grade	clear when solvented - white in emulsion - clear on drying	varies with solvent and grade	varies with solvent, grade, and solution	better used as solvented resins - see product literature
	CM Bond Series Conservator's Emporium 100 Standing Rock Circle Reno, NV 89511	1.455-1.470	varies with grade	white in emulsion - clear yellow on drying	varies with grade	varies with grade	see product literature M-1, 2, 3, 4
	Jade Series Jade Adhesives 2929 Campbell Avenue Chicago, IL 60618 #403, 454, others	1.455-1.470	varies with grade	white in emulsion - clear yellow on drying	varies with grade	varies with grade	see product literature

SOME RESINS USED IN CERAMIC AND GLASS REPAIR

CLASS	NAME/ADDRESS	RI	Tg	APPEARANCE	SET-TIME	VISCOSITY	NOTES
	Elvace Series (DuPont) TALAS 213 West 35th Street New York, NY 10001-1996 1874, others	1.455-1.470	varies with grade	white in emulsion - clear on drying	varies with grade	varies with grade	see product literature
ACRYLIC MONOMERS	Technovit 4004-A Rupert & Co., Ltd. Dennings Road Cheadle, Cheshire	1.495		clear	9 minutes Pot life - 3-5 minutes		very hard and glassy - good adhesion to glass - exothermic - dries cloudy

MATERIALS

DIVISION OF CONSERVATION

OBJECT CONSERVATION REPORT

Object No.:
Object: Glass Chandelier
Provenance: United Kingdom
Date: 1730-1740
Examined By: Deborah Long
Examination Date: 7/14/93

DESCRIPTION:

The object is a large colorless lead glass chandelier 127 cm in height, with twelve branches (or arms) in a single tier. Components are listed below from top to bottom. The shaft (or stem) of the chandelier holds ten clear glass faceted elements, of which six are above the level of the arms and three are below, terminating in a solid cut glass double acorn shaped element. Starting from the top the six upper elements fall into the following order: a small baluster-shaped element, a small flattened globe, a small globe, a medium sized inverted vase shaped element, a large globe, a medium sized flattened globe; all faceted excepting the uppermost element.

The console or receiver consists of two parts: a faceted hemispherical glass bowl shaped element and a copper alloy socket plate. The glass component has been silver gilt on the interior both to add brilliance and to obscure the ends of the branches from view. Together these two parts hold the branches in place by friction and counterweight. The twelve smooth round s-curved candle arms hold separate annular ribbed drip pans on small shoulders of glass attached to the bottom of each candle cup. At the other end of each branch is a copper alloy socket held in place with plaster.
Below the console, the four remaining elements are as follows: a faceted urn-shaped element, an unfaceted annular ribbed vase shaped element, a faceted vase shaped element, and the solid faceted glass terminal element.

Historical Information:

In the late seventeenth century, French chandelier makers began to use glass to produce "pendeloques" for brass chandeliers. Prior to this time quartz (rock crystal) had been used for these glittering elements. Glass used this way caught on quickly because it was less expensive and easier to fashion than quartz, and it

allowed makers to produce larger elements for their chandeliers. By the early eighteenth century, glass covered chandeliers were being offered for sale in London. The overall style remained similar to older brass lights until the middle of the eighteenth century. Glass chandeliers similar to 64.1009 were produced in England in about 1730-1740 and were fitted with cut glass elements which hid the central metal shafts and supported one or two tiers of solid s-curved glass branches. These chandeliers were sometimes referred to as "lustres" by some of the makers. Candle arms at this time were generally smooth and unfaceted.

Registrarial records indicate that this is the chandelier illustrated in Apollo, volume 26, no.154, p.216, October 1937; which was offered at that time by Messrs. Delomosne & Sons, Ltd. and may have hung before that time in Thornham Hall, Sussex, England. The small discrepancies in appearance between the chandelier in the illustration and the chandelier hanging in the Charleston Dining Room at Winterthur were discussed in letters between John Sweeney of Winterthur and R.J. Charleston of the Victoria and Albert Museum in 1964; and concerned mainly the difference in arrangement of the elements, and the blown glass terminal element then attached to the bottom of the chandelier.

CONDITION:

Overall, the condition of the chandelier is good. It appears to be structurally intact and stable. However, some of the individual parts of the chandelier are not stable and are detailed below, divided by type of element. Conditions are noted in order of severity of damage, from greatest to least in each section. Examination of the chandelier under ultraviolet light revealed a slightly greenish dull yellow fluorescence color emitted from all of the glass elements. The fluorescence color of two of the drip pans was slightly greener than the rest of the glass, as was the candle cup of branch number four.

Shaft Elements: The interior surface of the receiver bowl has an applied layer of silver. After XRF analysis failed to turn up any mercury, it was hypothesized that the bowl was water-gilded with geletin size. The silver layer is coated with a natural resin, which appears yellow to brown, has a definite crackle pattern, is extremely brittle, and fluoresces a dull yellow/orange. Conversations with Carol Aiken led to the supposition that the coating could be colophony (rosin), a pine resin byproduct typically found on reverse paintings on glass, and analytical results from FTIR spectroscopy confirmed that the closest computer match to this coating is a modern rosin sample from Fisher Scientific. The spotty deterioration of the silver seems to have been caused when embrittlement of the coating (which is highly crystalline) led to its failure and loss, allowing air to reach the unprotected silver. Subsequent corrosion caused complete loss of silver in many small spots with rings of corrision surrounding

glass surfaces. It is possible that the application of the hot wax to the candle cups during electrification caused some of the damage to the arms, particularly the breaks and cracks in and around the candle cups.

Drip Pans: The worst damage is to a single drip pan, which had approximately 30% of the rim broken off. This break was repaired originally with staples, and so has staple holes drilled into the rim. Opposite the break is a crack which appears to run completely through the body from the inner to the outer rim. Since the break has been repaired, it appears to be relatively stable.

Another pan has a large (20%) loss which has been filled with epoxy. The loss is connected to the inner rim with a crack. It is stable, but unsightly.

One of the pans has a large portion of the inner rim missing. This loss has been filled with polyester resin. The repaired area appears to be stable, but has yellowed badly.

Three of the pans have small chips and conchoidal losses at the inner rim. One of the three has a blind crack extending from the largest chip, and has been stabilized with epoxy resin, which has yellowed.

Six pans are in very good condition, having only minor chips around the inner rim; although three of these have had holes drilled in them in the past to accomodate other elements.

Overall the chandelier is covered with dust, dirt, and fingerprints.

Conservation records indicate that there have been two repair campaigns undertaken by Winterthur conservators. In 1976 at the request of the curator, Arlene Palmer, the chandelier was taken apart and the central shaft elements were cleaned and rearranged by Don Heller. He also altered the base of the shaft and replaced the lowest glass element, although there is no record of where the replacement part came from. Conversations with Don indicated that the original element was found in ninth floor storage by Ms. Palmer and given to him to put back on the chandelier.

The drip pan with the old stapled repair was taken apart, the staples were discarded, and the glass was adhered with "Ren Epoxy" by Andrew Lins. Also filled with the same epoxy at that time were two losses along the inner rims of two of the drip pans.

The large loss in the outer rim of one of the drip pans was filled with "Clear Cast" polyester resin. In 1988, this large fill had yellowed to the point where it became visually disturbing and it was removed by Claudia Deschu. She made a new fill with Hxtal NYL epoxy toned with dry pigments.

the loss areas. Presently, the silver is brittle and fragile where it is corroding but stable where the coating remains. Areas of loss were replaced with aluminum leaf at some point in the past. The leaf appears to have been stuck down with cellulose nitrate resin (fluorescing a bright blue/white). The aluminum leaf is not well adhered at the edges or in areas of overlap and there are places where all the layers have been scraped away. A second repair campaign employed a silvery paint (also analysed as aluminum), which appears to have been applied to losses near the center of the bowl in the more recent past.

The copper alloy socket plate has black surface corrosion, particularly at the outer perimeter; and there is some overall tarnishing in a spotty pattern. Examination under ultra-violet light showed what seemed to be a shellac coating (orange fluorescence) on the upper surface of the plate. When the chandelier was electrified holes were drilled through this plate to allow wires to pass up through the central shaft.

There are numerous small chips and losses along the edges of the glass shaft elements. The steel shaft shows moderate corrosion to the surface and may not be original, according to Don Heller. An outer sleeve of silver plated copper alloy has been fabricated to provide support to the glass elements without stressing the inner rims. Below the socket plate there is no steel support rod, only the plated copper alloy.

Branches: Two of the arms have old metal repairs where the candle cups meet the ends of the arms. One of these repairs (arm #12) is lead alloy and the other (arm #2) is a white metal which appears to be Monel metal or white brass. The arm with the lead repair also has a slim lead ring surrounding the candle cup which supports an adhesive repair. The cup is broken in half vertically and the adhesive has failed, leaving only the ring holding the cup together. Arm #8 has a vertical break repaired with a lead band and adhesive in a manner very similar to arm #12, although it has a three part break.

On arm #4 the candle cup has been replaced and is being held in place with a nut and bolt embedded in it's base. Arms #5 and #11 have 40% losses in the drip pan support shoulders at the base of the candle cups. On arm #7 the shoulder is a separate component and there is a 2 sq cm conchoidal loss at the base of the candle cup.

Arm #1 has a 1cm chip in the rim of the candle cup. Arm #6 has a vertical blind crack in the side of the candle cup. Arms #3, #9, and #10 are in very good condition, having only minor chips in the rims of the candle cups.

The chandelier has been electrified with false candles secured in the cups with wax and electrical wires which were glued to the

Solvent Testing:

Solvent tests indicated that both the Hxtal epoxy resin and the yellowed polyester resin softened in methylene chloride. The glue used to hold the wiring in place, probably a cellulose nitrate glue, was soluble in both acetone and ethanol, as was the older adhesive in the candle cup breaks. The corrosion products on the resin coated copper alloy socket plate could be reduced with both citric and formic acids without damaging the shellac coating. CAL glass cleaning solution easily cleaned the surface of the glass.

All of the applied coatings on interior of the receiver bowl were soluble in acetone, and their removal does not affect the silvering on the surface of the glass.

TREATMENT OBJECTIVE:

Although the chandelier is generally sound, there are some things that could be done to improve both its structural stability and its appearance. There are some large cracks and breaks that need repair to maintain the structural stability of some of the components. The silvering inside the console is unstable and should get attention. Both the socket plate and the central shaft are corroding. Additionally, there are aesthetic concerns that need to be addressed prior to exhibition, such as the unsightly polyester and epoxy repairs. This object is to be placed in the "Eye for Excellence" exhibit in the Gallery.

TREATMENT PROPOSAL:

1. Dis-assemble the central chandelier shaft, noting the location of each section in the attached drawing.

2. As directed by the curator, de-electrify and remove false candlesticks by soaking the branches in petroleum benzine. As the wax is softened, carefully remove the candles from the glass sockets.

3. Mechanically remove lead rings from the broken candlecups and remove old discolored adhesive with acetone.

4. Remove discolored epoxy and polyester adhesives and fill materials with Zip-Strip (a proprietary paint stripper comprised of 80% methylene chloride, <10% ethanol, 5% mineral spirits, <4% methanol, in a proprietary gel medium; Star Bronze Company, Alliance, Ohio), repeating if necessary until all the material has been removed.

5. Clean all the glass parts in CAL glass cleaning solution (50/50 ethanol and distilled water, adjusted to ph 9 with ammonium

hydroxide) and dry thoroughly.

6. Clean glass edges to be joined, using acetone on cotton swabs, and secure sections with scotch tape. Wick Epotek 301-2 (Epoxy Technology, 14 Fortune Dr., Billerica, MA) epoxy resin into the cracks and allow it to cure at ambient temperature and humidity. After cleaning with acetone, attempt to pull Epotek into the blind crack on branch # 6. This epoxy has been chosen both for its high index of refraction (1.564), and its low viscosity.

7. Use Dow corning Silastic T silicone rubber to make molds of complete sections of both the drip pan and the candle cups with losses, and apply to areas of loss. Silastic T was chosen both for its minimal shrinkage and its compatibility with epoxy resins. It is also transluscent, which may make alignment on the object easier. Provide an extra space at the top of the mold to allow for shrinkage during the cure time. Pour in Epotek 301-2 epoxy resin toning, only if needed, with Orosol dyes (Ciba-Geigy Inc.)to match the color of the glass. Allow the epoxy to cure before removal of the molds, remove, and carve or sand and polish the fills as needed.

8. Clean the central iron rod by ~~blasting~~ abrasive at 40psi with 60/200 mesh crushed walnut shells. If necessary, any remaining corrosion products can be removed by applying CRC 3-36 (CRC Industries, Warminster, PA), a proprietary penetrating oil composed of petroleum distillate (67%), an inhibited paraffinic oil (29%), and carbon dioxide (4%). Allow the CRC to soak for several hours and brush with a fine glass bristle brush to remove loosened corrosion products. Remove excess CRC and glass particles from the surface of the iron with petroleum benzine and a soft cloth, and apply a coat of paste wax (100g BeSquare 195° microcrystalline wax, 25g Polywax 2000, 200ml mineral spirits), buffing with a stiff natural bristle brush.

9. Clean the copper alloy arm socket plate and socket ends by first degreasing with petroleum benzine, then applying 2% Igepal A630 (Talas,) in distilled water to remove surface dirt, rinsing with water, and applying either 10% diammonium citrate or 5% formic acid, depending on the level of corrosion, to the areas of heavy corrosion, rinsing with distilled water, and drying thoroughly. Chemically dry with acetone. Apply two coats of Acryloid B48S (Rohm & Haas, Philadelphia, PA), 10% in xylene, followed by a coat of paste wax (as above).

10. From the standpoint of the long-term stability of the object as a whole, and due to the badly degraded condition of the colophony, the curator decided to view the colophony in the same way painting varnish is viewed - as strictly a protective coating with no aesthetic importance, to be renewed as necessary for the protection of the silver. Since the solubility parameters were so similar, it was decided to remove all of the old coatings and

aluminum leaf with acetone. An isolating layer of Acryloid B-72 10% in acetone will be applied, and the loss areas will be re-leafed with new silver, burnishing as needed to approximate the appearance of the original material. The new leaf will be coated with the same acrylic to protect it from corrosion.

11. Arms #2 and #12 have stable but somewhat unattractive repairs. X-radiography would be helpful in determining the extent of loss to the glass under the repairs (although this can be done only on the arm with the copper alloy repair). The decision of the curator is to take the old repairs apart mechanically and replace them with epoxy fills as above, dowelling if necessary with glass rod to provide increased structural stability.

12. The arm with the dowelled and screwed candle cup, while loose and movable, appears to have been done to compensate for lateral deformation in the arm and may have been done by the original glassmaker to avoid having to make another arm. Cleaning with acetone and adhering the two pieces with Acryloid B-72 50% in acetone should serve to stabilize the parts and minimize the visual interference of the old repair while leaving it intact.

13. Clean all the replacement silver-plated copper alloy sleeves with acetone and apply two coats of Acryloid B-48 (as above). Paste wax (as above) to provide slip when fitting the parts back together. Reassemble chandelier.

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Submitted By:

_____ 9/29/93
Date

Approved By:

_____ 9/30/93
Objects Conservator Date

_____ 9/30
Director of Conservation Date

_____ _____
Curator Date

EPOXY TECHNOLOGY

DATA SHEET

EPO-TEK.

301-2

Optically Transparent Epoxy

Rev. III
11/96

SPECIFICATIONS

NUMBER OF COMPONENTS ..... Two

MIXING RATIO ..... PARTS BY WEIGHT
- Part "A" ..... 100 gms.
- Part "B" (hardener) ..... 35 gms.
- NOTE: If Part "A" crystallizes in storage, merely place container in a warm oven (without cap) until crystallization disappears. Allow to cool to room temperature before mixing with the Part "B" (hardener).

CURING SCHEDULE
- 80°C ..... 1½ hours
- Room Temperature ..... 2 days

OPTICAL PROPERTIES
- Index of Refraction 1.564
- 90% transmission at 3000 angstroms
- 98-99% transmission at 3100 angstroms to 2.5 microns

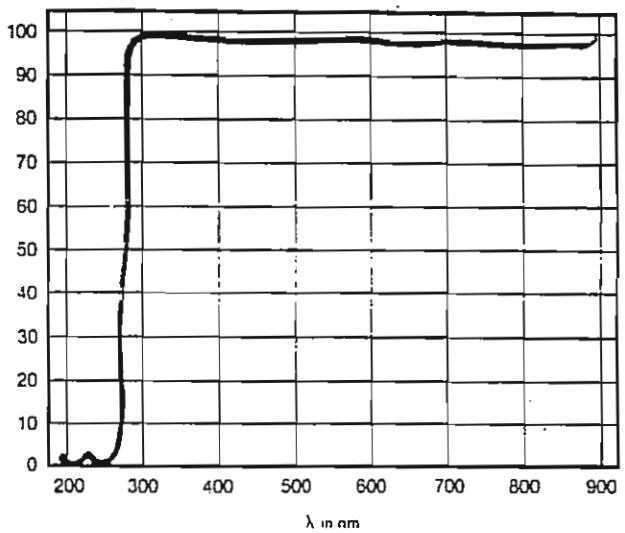
PHYSICAL PROPERTIES
- Color ..... Clear
- Specific Gravity 0.95
- Viscosity (mixed) @ 100 rpm/23°C ..... 300 - 600 cPs
- Hardness, Shore D 82
- Glass Transition Temp. (Tg.) cured @ 80°C/3 hours ..... > 65°C
- Operating Temperature Range ..... -45°C to 200°C
- Water Absorption (30 days; 94% RH; @ Room Temp.) 0.01%
- Moisture Resistance (10 days; 94% RH; -10°C to 65°C MIL-STD 750 Test 1021.1). Passed
- Weight Loss; 200°C - 300 hours 0.07%
- Coefficient of Linear Thermal Expansion (30°C-90°C) 62 x 10^{-6} in/in/°C
- Linear Shrinkage 1.4%
- Temperature Cycling (epoxy on ceramic) MIL-STD 750; Test 1051.1 ..... Passed
- Thermal Shock (epoxy on ceramic) MIL-STD 750; Test 1051.1 ..... Passed
- Lap Shear Strength (Al to Al) ..... 2,000 psi

ELECTRICAL PROPERTIES
- Dielectric Strength ..... 500 V/mil
- Dielectric Constant 25°C; 100 KC 3.1
- 115°C; 100 KC 3.67
- Volume Resistivity (ohm-cm) ..... >3.5 x 10^{14}
- Dissipation Factor 0.038

POT LIFE ..... One(1)day

SHELF LIFE
- One (1) year when stored at room temperature. Keep container closed when not in use.

REFRIGERATION IS NOT REQUIRED.



EPO-TEK 301-2

INSTRUMENT: PE320
SOURCE: W/Deut.
SANDPASS: Variable

REFERENCE: Quartz
SAMPLE: .0015" between two quartz plates

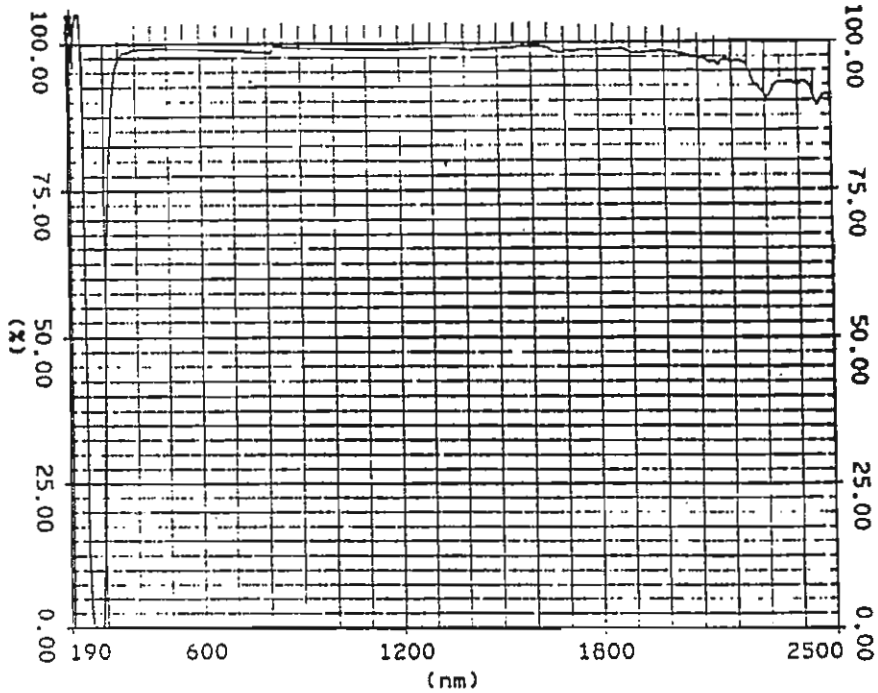
EPO-TEK 301-2 is a two component epoxy that can be cured with or without heat. In addition to its excellent optical properties, the 301-2 is a clear epoxy that has a low viscosity, long pot life (8 hrs.) and good handling characteristics. It was designed for optical applications such as a lens for optoelectronic display devices, bonding fiber optics (glass or plastic) and, for optical filters. EPO-TEK 301-2 can be used for bonding glass, quartz, metals and most plastics. It has also been used for impregnating wooden objects in the restoration of artifacts.

The maximum recommended service temperature is 125°C.

NONTOXIC - complies with USP Class VI Biocompatibility Standards.

EPOXY TECHNOLOGY, INC. [illegible] USA
PHONE [illegible] FAX [illegible]

EPOXY TECHNOLOGY



SAMPLE : 301-2 REFERENCE : GLASS
CONC. : N/A PATHLENGTH :
COMMENT :

[FIXED] WAVELENGTH	(%T) VALUE	[FIXED] WAVELENGTH	(%T) VALUE
1: 2500.0	90.76	2: 2450.0	90.56
3: 2400.0	92.64	4: 2350.0	92.98
5: 2300.0	90.73	6: 2250.0	95.52
7: 2200.0	96.29	8: 2150.0	96.59
9: 2100.0	97.17	10: 2050.0	97.89
11: 2000.0	98.37	12: 1950.0	98.19
13: 1900.0	98.29	14: 1850.0	98.74
15: 1800.0	98.59	16: 1750.0	98.66
17: 1700.0	98.23	18: 1650.0	99.04
19: 1600.0	99.31	20: 1550.0	99.07
21: 1500.0	98.98	22: 1450.0	98.77
23: 1400.0	98.88	24: 1350.0	99.07
25: 1300.0	99.11	26: 1250.0	98.97
27: 1200.0	98.84	28: 1150.0	98.81
29: 1100.0	98.88	30: 1050.0	98.89
31: 1000.0	98.97	32: 950.0	99.10
33: 900.0	98.81	34: 850.0	99.29
35: 800.0	98.46	36: 750.0	98.59
37: 700.0	98.78	38: 650.0	98.87
39: 600.0	99.04	40: 550.0	99.18

SPEED : MID. SLIT : 5.0
DATE : 9-6-88

ANALYST : CTM

EPOXY TECHNOLOGY

DATA SHEET

EPO-TEK

301

Spectrally Transparent Epoxy

Rev. I
1/94

SPECIFICATIONS

NUMBER OF COMPONENTS ..... Two

MIXING RATIO — PARTS BY WEIGHT
- Part "A" 20
- Part "B" (hardener) 5
- Maximum recommended mixed quantity should not exceed ..... 25 grams

CURE SCHEDULE (Bond line temperatures - use any one of the following)
- 65°C ..... 1 hour
- Room temperature ..... Overnight

OPTICAL PROPERTIES (Adhesive film thickness-0.0035")
- Greater than 97% transmission 3200 - 9000 Å
- Greater than 80% transmission 9100Å - 2.6µ

INDEX OF REFRACTION ..... 1.538 - 1.540

PHYSICAL PROPERTIES
- Lap Shear Strength ..... 1700 psi (aluminum to aluminum)
- Specific Gravity (A & B mixed) 1.09
  - Part "A" 1.15
  - Part "B" 0.87
- Shore D Hardness 81
- Glass Transition Temperature (Tg) (Cured @ 65°C/1 hour) ..... 48°C
- Coefficient of Thermal Expansion
  - Below Tg: 50×10^{-6} in/in/°C
  - Above Tg: 125×10^{-6} in/in/°C

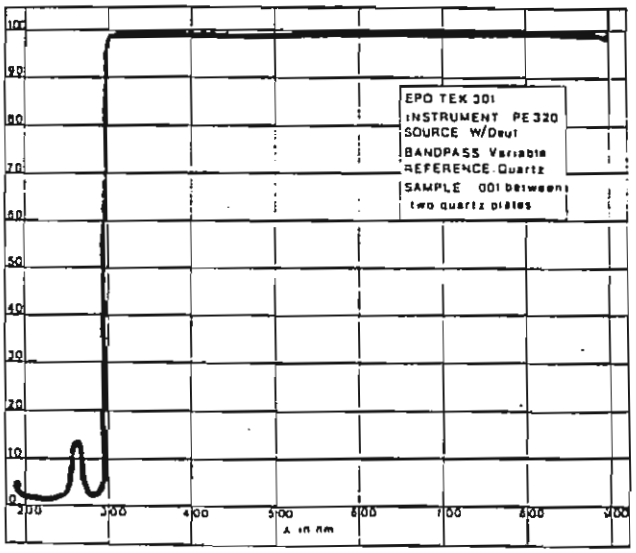
OUTGASSING PROFILE FOR AEROSPACE ENVIRONMENT
- Total weight loss by weight (%) 1.08
- VCM (volatile condensable materials) % by weight 0

VISCOSITY (25°C)
- Parts "A" & "B" mixed ..... 100 cps

POT LIFE
- 100 gram sample ..... 30 min.
- 25 gram sample ..... 50 min.

SHELF LIFE
- One year when stored at room temperature. Keep containers closed when not in use.

REFRIGERATION NOT REQUIRED



EPO-TEK 301 is a two component, room temperature curing, epoxy adhesive featuring very low viscosity, good pot life, good handling characteristics and excellent optical properties.

Although designed primarily for optical filters, EPO-TEK 301 has found wide usage in many instrumentation applications. It is also recommended for bonding glass and plastic fiber optics.

EPO-TEK 301 has good adhesion to many different types of substrates including glass, quartz, metals and most plastics.

Based on outgassing test results by NASA, EPO-TEK 301 is approved for space flight programs.

NONTOXIC - complies with USP Class VI Biocompatability standards

EPOXY TECHNOLOGY, INC. [illegible]
PHONE: [illegible] FAX: [illegible]

PLASTICS WORLD

Adhesive transmits light

Epoxy safe to use with plastics since no solvents are necessary

A two-component epoxy is being used effectively for thin-film interference filters and for the bonding of lenses and other substrates.

"Epo-Tek 301", made by Epoxy Technology, has the unique properties of being optically transparent between 3000 angstroms and 2.6 microns and bondable to most glasses, metals, ceramics and plastics. According to end user, Corion Instruments, a special advantage is gained by its having a refractive index closely matching most of the common glasses.

Several glass elements may be cemented together with the new epoxy with the total transmission being increased considerably when compared with the same elements arranged in air-gap sequence. Another noteworthy gain is freedom from yellowing in intense ultraviolet light at high temperatures.

This adhesive is useful for making microsection studies of rocks, animal tissue and various other materials because of the following properties: (a) very low viscosity, (b) room-temperature curing, (c) toughness and adhesion and (d) index of refraction same as glass.

(Continued)

Medical slides sandwiched between glass that is joined with "Epo-Tek 301" are hermetically sealed and protected with no reflecting interior surfaces to hamper visibility and clarity.

"Epo-Tek 301" has been used for replicating optical components such as mirrors because of its combination of desirable properties. Because the material is a 100-percent solids formulation, requiring no solvents, it does not attack most plastics. Its curing time is controlled accurately as a function of temperature.

Although the spectral range of the cement's transparency is very broad, its light cut-on characteristics are extremely sharp. This property is utilized in some types of Corion filters, making the epoxy perform both an optical and a mechanical function.

Corion and Epoxy Technology jointly have developed a new, optically opaque black epoxy compound. Even when applied in a thin film, it still transmits less than 0.0001 percent over the wavelength range of 3000 angstroms to 1 micron. This is used to mask out certain areas where light transmission is undesirable. The high epoxy bonding strength joins the opaque coating and the optical substrate into a single entity, with separation virtually impossible.

These achievements emphasize the benefits to be derived from joint and inter-disciplinary R&D efforts between plastics makers and product specialists. In this case, the cooperative effort was made by Epoxy Technology, a supplier of custom-formulated epoxy compounds, and Corion Instruments, which specializes in thin-film deposition of metals and other materials on glass and quartz.

Reprint: PLASTICS WORLD
Feb. 1969

Information About High Technology Products

DOW CORNING

SILASTIC® L RTV Silicone Rubber

Type	Two-part silicone rubber
Physical Form	
as supplied	Pourable fluid
as cured	Flexible rubber
Cure	24 hours at room temperature, or cure time can be accelerated with heat
Special Properties	Excellent flexibility and long mold life, high elongation, stretches rather than tearing
Primary Uses	For flexible molds with deep undercuts and general potting and encapsulating applications

DESCRIPTION

SILASTIC® L RTV silicone rubber is a two-part, room-temperature-/addition-reaction-curing silicone rubber designed for use as a flexible mold-making and general potting and encapsulating material. Its superior elongation, low modulus and high strength characteristics combine to make an excellent material that minimizes tear, improves part removal ease, and provides longer mold life and nil shrinkage when cured at room temperature.

With curing agent added, SILASTIC L RTV silicone rubber base becomes a pourable fluid capable of filling the most minute crevices and reproducing intricate details. Cured, its superior elongation makes it ideal for minimizing tears when parts with deep undercuts and close tolerances are reproduced.

HOW TO USE

Pattern Preparation

Certain contaminants sometimes used in moldmaking operations can prevent SILASTIC L RTV silicone rubber from curing. Patterns to be molded should be thoroughly cleaned to remove grease, oil and other surface contaminants. Care should also be taken to ensure that corners, crevices and draws are free of dirt or particles of foreign matter. A light "blow over" with compressed air is advised when the pattern has convoluted draws or undercuts. Then the original model or pattern should be placed in a light frame of cardboard, foil, wood or other material. There should be approximately 1/4-inch clearance on all sides and over the top of the pattern. The pattern should be attached securely to the bottom of the frame so it does not float.

A pattern release agent should then be wiped or sprayed on the pattern. Spreading a light coat of release agent on the sides and underside of the top of the frame will facilitate release.

A good pattern release agent can be made by making a 5 percent solution of petroleum jelly in a suitable solvent. Either VM&P naphtha or mineral spirits can be used.

CAUTION: When handling solvents, always provide adequate ventilation. Keep away from heat, sparks and open flames. Always follow all precautions given on the solvent container label, and ensure compliance with local, state and federal regulations.

Addition of Curing Agent

SILASTIC L RTV silicone rubber base and its curing agent are produced in matched lots; the two parts should be used in the kit form, as supplied. For the best curing results, use metal cans, clean glassware or unwaxed paper containers for mixing the base and curing agent. SILASTIC L RTV silicone rubber curing agent should be mixed into the base material just before use (with either manual or mechanical stirring) in the amount of one part curing agent to ten parts base by weight. Inclusion of air during mixing may cause voids in the finished mold. Entrapped air may be removed by applying a vacuum of 28 to 29 inches of mercury. Under such a vacuum, the material will expand four to five times its original volume. As the froth collapses, the mixture will recede to its original volume. The vacuum should be held one or two minutes longer before releasing. Pressure casting may be substituted with equal success.

Working Time

Unlike conventional organotin catalyzed RTVs that double or triple viscosity immediately after the curing agent is added, SILASTIC L RTV silicone rubber remains a flowable, pourable material for 2½ hours after the curing agent is added.

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TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied		
CTM 0176[1]	Appearance, Base	Buff
	Curing Agent	Dark green
	Base to Curing Agent Mixing Ratio, by weight	10:1
As Catalyzed		
CTM 0176	Appearance	Green
CTM 0050	Viscosity[2] at 25 C (77 F), poise	925
CTM 0092A	Snap Time[3] at 25 C (77 F), hours	2.5
CTM 0092A	Cure Time[4] at 25 C (77 F), hours	24
	at 65 C (150 F), minutes	30
	at 100 C (212 F), minutes	15
	at 150 C (302 F), minutes	5
As Cured – Physical Properties[5]		
CTM 0099	Durometer Hardness, Shore A, points	35
CTM 0137A	Tensile Strength, psi	550
CTM 0137A	Elongation, percent	350
CTM 0159A	Tear Strength, Die B, ppi	65
CTM 0022	Specific Gravity at 25 C (77 F)	1.28
CTM 0157	Linear Shrink	Nil
CTM 0224	Thermal Conductivity, Cal-cm/sec-sq cm/°C	6.6×10^{-4}
CTM 0585	Volume Coefficient of Thermal Expansion, cc/cc/°C (0-100 C)	10.2×10^{-4}
Electrical Properties[6]		
CTM 0114	Dielectric Strength, volts/mil	500
CTM 0112	Dielectric Constant	
	at 100 Hz	2.71
	at 100 KHz	2.75
CTM 0112	Dissipation Factor	
	at 100 Hz	0.0088
	at 100 KHz	0.0026
CTM 0249	Volume Resistivity, ohm-cm	4.66×10^{14}
CTM 0249	ARC Resistance, seconds	122

[1]In most cases, CTMs (Corporate Testing Methods) correspond to ASTM standard tests. Copies of CTM procedures are available upon request.

[2]Brookfield Viscometer Model HAF, spindle #6 at 5 rpm.

[3]Time required to become nonflowable.

[4]Based on sample mass of one cubic inch.

[5]Based on sample thickness of 125 mils, cured 24 hours at 25 C (77 F).

[6]Based on sample thickness of 75 mils, cured one hour at 150 C (302 F).

Specification Writers: Please obtain a copy of the Dow Corning Sales Specification for this product, and use it as a basis for your specifications. It may be obtained from any Dow Corning Sales Office, or from Dow Corning Product Information in Midland, MI. Call (517) 496-6000.

Curing

The cure of SILASTIC L RTV silicone rubber occurs by a reaction between the base polymer and the curing agent. This polymerization requires 24 hours after the addition of the curing agent at room temperature. This material will not revert or depolymerize, even under conditions of elevated temperature and confinement. Vulcanization can be accelerated by heating the catalyzed material. However, this will increase the shrinkage from nil to 0.3 percent. A part 1/4-inch thick will set up within 30 minutes if the temperature is maintained at 65 C (150 F). The rate at which thicker sections will set up depends on the size and shape of the piece.

Vulcanization will not be accelerated at the center of the piece until the entire mass has reached the elevated temperature. Average set-up times at various temperatures for 1/4-inch moldings are:

Temperature	*Set-Up Time*
25 C (77 F)	<24 hrs.
52 C (125 F)	60 min.
65 C (150 F)	30 min.
93 C (200 F)	15 min.
121 C (250 F)	7 min.
149 C (300 F)	5 min.

Inhibition

Localized inhibition of cure may be encountered at the interface when SILASTIC L RTV silicone rubber, during the curing process, comes in contact with certain contaminants. Among materials found to cause inhibition are sulphur-containing and organometallic salt-containing compounds, such as organic rubbers, and many RTV silicone rubbers.

Surfaces previously in contact with any of the above materials may also cause inhibition. If in doubt, test for compatibility by brushing a small amount of catalyzed SILASTIC L RTV silicone rubber over a localized area of the surface to be reproduced. Inhibition has occurred if the rubber is gummy or uncured after the curing period has elapsed.

Inhibitors

The following materials have been checked for compatibility with SILASTIC L RTV silicone rubber. Inhibitors include:

DOW CORNING® 3100 series and DOW CORNING® HS series RTV silicone rubbers

DOW CORNING® 282 adhesive

MARBLEX®[1] clay

Polysulfied MIL-S-8516

Epoxy-amine cured

SCOTCH®[2] cellophane tape

PERMACEL®[3] masking tape

Neoprene rubber

Buna N rubber

Natural rubber

Polyvinylchloride-plasticized

THERMOSET®[4] Epoxy 619 with 619 hardener

THERMOSET®[4] Epoxy 200 with EI 869 hardener

MARASET®[5] Epoxy 656 with 656 hardener

SHERWIN-WILLIAMS[6] oil stain

Laminac polyester

Noninhibitors

The following materials have been checked for compatibility with SILASTIC L RTV silicone rubber. Noninhibitors include:

KINDT-COLLINS™[7] sheet and fillet wax

FREEMAN[8] Supply Company sheet and fillet wax

Permaplast X33 clay

KLEAN KLAY[9] #20

U.S. Gypsum-Hydracal

Epoxy-Anhydride cured

REAPOXY-77 with hardener A

DURHAM'S ROCK HARD[10] water putty

Vel-mix stone

POLYLITE[11] 32-180 polyester

POLYLITE[11] 32-112 polyester

POLYLITE[11] 93-541 polyester

POLYLITE[11] 34-843 polyester

SCHALK[12] water putty

PRATT & LAMBERT[13] spray enamel

BOYLE-MIDWAY® PLASTIC WOOD[14]

THERMOSET[4] Epoxy 609 with 609 hardener

POLYFORM[15] modeling clay

Staples WOODTONE™[16] putty (latex)

SHIPPING LIMITATIONS

None.

STORAGE AND SHELF LIFE

SILASTIC L RTV silicone rubber and its curing agent should be stored in closed containers at or below room temperature. The materials have a shelf life of 6 months from date of shipment.

PACKAGING

SILASTIC L RTV silicone rubber is supplied with SILASTIC® L RTV curing agent in matched-lot, 1.1-, 9.9-, 49.5- and 495-lb (0.5-, 4.4-, 22- and 224-kg) kits. All weights, net.

MSDS INFORMATION

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MIDLAND, MICHIGAN 48686-0994

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DOW CORNING

Information About *Silastic*® T-2 Silicone Moldmaking Rubber

Type
Two-component, high-strength, silicone moldmaking rubber

Appearance
Translucent

Special Properties
Low viscosity, very fast cure with heat, high inhibition resistance and very low shrinkage

Primary Uses
For detailed reproduction of surfaces and objects for prototype design, production tooling, and artistic and renovation applications

DESCRIPTION

Silastic® T-2 Silicone Moldmaking Rubber is a translucent, high-strength silicone moldmaking rubber for detailed reproduction of surfaces and objects for prototype design and production tooling, as well as artistic and renovation applications. It is a two-component material consisting of a base and a curing agent, which when mixed, cure at room or elevated temperatures by an addition reaction. It is translucent, allowing molds to be cut without fear of damaging masters, and also allowing pigmentation to meet individual coloration needs.

FEATURES

- Low viscosity for easy mixing and deairing
- Very fast cure with heat
- High inhibition resistance
- Very low shrinkage
- Medium range durometer hardness
- Translucent/colorless

HOW TO USE

The surface of the original should be clean and free of loose material. When correctly mixed with the curing agent, *Silastic* T-2 Moldmaking Rubber releases well from most substrates after cure. With porous substrates, a release agent or barrier coat may be needed to seal the surface before casting the silicone. Release coatings such as petroleum jelly or others can be used. Before casting the silicone rubber, it is advisable to verify that no adhesion has occurred between the *Silastic* T-2 Moldmaking Rubber and the master mold or frame.

APPLICATION

Weigh out 100 parts of *Silastic* T-2 Translucent Base and 10 parts of *Silastic* T-2 Curing Agent in a clean container. Mix until the curing agent is completely dispersed in the base. Mix suitably small quantities to ensure thorough mixing of the base and curing agent and adequate working time.

Entrapped air should be removed in a vacuum chamber, allowing the mixture to completely expand and then collapse. After an additional five minutes, the vacuum can be released. A volume increase of **four to five times** will occur upon vacuum deairing of the mixture, so a suitably large container should be chosen.

Pour the mixed base and curing agent onto the master, avoiding air entrapment. Some bubbles will remain in the material after vacuum deairing – these will rise to the surface and break during the working time. The material should be allowed to stand for about 30 minutes at room temperature after deairing and before heat curing. The catalyzed mixture will cure in thick sections to a flexible rubber; typically within 12 hours at room temperature, at which time the part can be demolded. Heat will greatly accelerate the cure. There may be some contraction upon cooling due to the coefficient of thermal contraction differences between the silicone rubber and the original. The higher the curing temperature, the greater the differences in dimensions.

Working and Cure Times

Temperature °F	Temperature °C	Typical Working Time, Minutes	Typical Time to Cure
68	20	180	14 hours
77	25	140	10 hours
86	30	105	7 hours
95	35	65	4 hours
104	40	35	2 hours
122	50	15	45 minutes

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INHIBITION OF CURE

All addition cure silicone elastomers are susceptible to cure inhibition when in contact with certain materials and chemicals. It is strongly recommended that mixing containers, mold construction materials, masters and release agents be checked for any inhibition effect before use by properly mixing *Silastic* T-2 Translucent Base and its curing agent and applying a small amount against the surfaces. Inhibition has occurred if the elastomer is only partially cured after 24 hours, or has a sticky surface in contact with another material. Amines and sulfur-containing materials are strong inhibitors, as are organotin salts used in condensation cure silicones. Wet or moist surfaces can cause gas bubbles to form during cure in the silicone adjacent to the substrate surface.

LIMITATIONS

Not intended for medical use.

SHIPPING LIMITATIONS

None.

STORAGE AND SHELF LIFE

Silastic T-2 Translucent Base and its curing agent should be stored in closed containers at or below room temperature. The materials have a shelf life of six months from date of shipment. Ensure that containers are tightly closed after use.

PACKAGING

Silastic T-2 Translucent Base is available in 9, 45 and 440 lb (4, 20 and 200 kg) containers. *Silastic* T-2 Curing Agent is available in 0.9, 4.5 and 44 lb (0.4, 2 and 20 kg) containers.

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied	
Base Color	Translucent
Viscosity, centipoise or mPa.s	50,000
Curing Agent Color	Transparent
Viscosity, centipoise or mPa.s	550
As Mixed: 100 Parts Base to 10 Parts Curing Agent by Weight	
Viscosity, centipoise or mPa.s	40,000
Specific Gravity	1.12
As Cured: 24 hours at 77°F (25°C)	
Durometer Hardness, Shore A	42
Tensile Strength, psi	800
Elongation, percent	300
Tear Strength, Die B, ppi	120
Linear Shrink, percent	<0.1

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Dow Corning Corporation
Midland, Michigan 48686-0994

DOW CORNING

Information About High Technology Products

DOW CORNING

DESCRIPTION

SILASTIC® E RTV silicone rubber is a two-part silicone rubber designed for use as a flexible moldmaking and general potting and encapsulating material. This high-strength, tear-resistant silicone rubber cures at room temperature with an addition-reaction cure. SILASTIC E RTV silicone rubber offers easy release, high elongation and minimum shrinkage. Other outstanding characteristics include:

- Reversion resistance
- Long working time
- Heat-accelerable cure
- Wide service temperature range from -55 to 200 C (-67 to 392 F)

An easy-to-mix ratio of 10:1 base to curing agent ensures accurate measuring or blending by hand or machine. The material cures in unlimited thickness, regardless of part configuration or degree of confinement.

USES

Electrical/Electronic Applications

SILASTIC E RTV silicone rubber is an ideal electrical/electronic material for general potting and encapsulating of modules, relays, power supplies, amplifiers, transformers and connectors.

Moldmaking Applications

After mixing with its curing agent, SILASTIC E RTV silicone rubber becomes a pourable liquid capable of forming durable, flexible molds for producing parts with unusual configurations, severe undercuts and close tolerances.

SILASTIC® E RTV Silicone Rubber

Type	Two-part silicone rubber
Physical Form	
as supplied	Pourable liquid
as cured	Flexible rubber
Cure	At room temperature within 24 hours after addition of curing agent
Special Properties	High strength; tear resistance; low shrink; high elongation
Primary Uses	Flexible molds used to reproduce intricate detail; potting and encapsulating applications

HOW TO USE

Pattern Preparation

Patterns to be molded should be thoroughly cleaned to remove grease, oil and other surface contaminants. Certain contaminants sometimes used in moldmaking operations can prevent SILASTIC E RTV silicone rubber from curing. Care should also be taken to ensure that corners, crevices and draws are free of dirt or particles of foreign matter. A light "blow over" with compressed air is advised when the pattern has convoluted draws or undercuts. Then place the original model or pattern in a light frame of cardboard, foil, wood or other material. Allow approximately 1/4-inch clearance on all sides and over the top of the pattern. Attach the pattern securely to the bottom of the frame so that it does not float.

A pattern release agent should then be wiped or sprayed on the pattern. A light coat of release agent on the sides and underside of the top of the frame will facilitate release.

Addition of Curing Agent

SILASTIC E RTV silicone rubber base and its curing agent are produced in matched lots; the two parts should be used in the kit form, as supplied. For the best curing results, use metal cans, clean glassware or unwaxed paper containers for mixing the base and curing agent. SILASTIC E RTV silicone rubber curing agent should be mixed into the base material just before use (with either manual or mechanical stirring) in the amount of one part curing agent to ten parts base by weight. Note: Varying the ratio of the SILASTIC E RTV curing agent will not hasten or slow the rate of cure. However, it will result in lowering the physical properties of the cured rubber. Inclusion of air during mixing may cause voids in the finished mold. Entrapped air may be removed by applying a vacuum of 28 to 29 inches of mercury. Under such a vacuum, the material will expand four to five times its original volume. As the froth collapses, the mixture will recede to its original volume. The vacuum should

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be held one or two minutes longer before releasing. Pressure casting may be substituted with equal success.

With the curing agent added, 1 lb (0.45 kg) of SILASTIC E RTV silicone rubber will produce 25 cubic inches (409.7 cubic centimeters) of rubber.

Working Time

Unlike conventional organotin-catalyzed RTV rubbers that double or triple viscosity immediately after addition of curing agent, SILASTIC E RTV silicone rubber remains a pourable material of less than 1500 poises for up to two hours after being mixed with its curing agent.

Curing

The cure of SILASTIC E RTV silicone rubber occurs by a reaction between the base polymer and the curing agent. This polymerization requires 24 hours after the addition of the curing agent at room temperature. This material will not revert or depolymerize, even under conditions of elevated temperature and confinement. Vulcanization can be accelerated by heating the catalyzed material. However, this will increase the shrinkage from nil to 0.3 percent. A part 1/4-inch thick will set up within 30 minutes if the temperature is maintained at 65 C (150 F). The rate at which thicker sections will set up depends on the size and shape of the piece.

Vulcanization will not be accelerated at the center of the piece until the entire mass has reached the elevated temperature. Average set-up times at various temperatures for 1/4-inch moldings are shown below:

Temperature	Set-Up Time
25 C (77 F)	<24 hrs
52 C (125 F)	60 min
65 C (150 F)	30 min
93 C (200 F)	15 min
121 C (250 F)	7 min
149 C (300 F)	5 min

Inhibition

Localized inhibition of cure may be encountered at the interface when SILASTIC E RTV silicone rubber, during the curing process, comes in contact with certain contaminants. Among materials found to cause inhibition are sulphur-containing and organometallic salt-containing compounds, such as organic rubbers, and many RTV silicone rubbers.

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied		
CTM 0176[1]	Appearance	
	base	White
	curing agent	Clear
	Mixing Ratio, base to curing agent, by weight	10:1
As Catalyzed – 10:1 Ratio, by weight		
CTM 0176	Appearance	White
CTM 0050	Viscosity[2] at 25 C (77 F), poise	600
CTM 0055	Pot Life[3], hours	2
CTM 0092A	Cure Time[4]	
	at 25 C (77 F), hours	24
	at 65 C (150 F), minutes	30
	at 100 C (212 F), minutes	15
	at 150 C (302 F), minutes	5
As Cured – Physical Properties[5]		
CTM 0099	Durometer Hardness, Shore A, points	33
CTM 0137A	Tensile Strength, psi	800
CTM 0137A	Elongation, Die C, percent	400
CTM 0159A	Tear Strength, Die B, ppi	100
CTM 0022	Specific Gravity at 25 C (77 F)	1.12
CTM 0157	Linear Shrink, percent	
	24 hours	Nil
	7 days	0.1
CTM 0224	Thermal Conductivity, Cal-cm/sec-sq cm/°C	4.35×10^{-4}
CTM 0585	Volume Coefficient of Thermal Expansion, cc/cc/°C (25-150 C)	8.7×10^{-4}
	Water Absorption[6], percent	0.10
	Specific Heat	$3.71 \times 10^{-4}\ Tc° + 3.201 \times 10^{-1}$
Electrical Properties[7]		
CTM 0114	Dielectric Strength, volts per mil	500
CTM 0112	Dielectric Constant	
	100 Hz	2.81
	100 kHz	2.82
CTM 0112	Dissipation Factor	
	100 Hz	0.006
	100 kHz	0.002
CTM 0249	Volume Resistivity, ohm-cm	5.0×10^{14}
CTM 0249	Arc Resistance, seconds	121

[1]In most cases, CTMs (Corporate Testing Methods) correspond to ASTM standard tests. Copies of CTM procedures are available upon request.

[2]Brookfield Viscometer Model HAF, spindle #6 at 5 rpm.

[3]Time required to double initial catalyzed viscosity.

[4]Based on sample mass of one cubic inch.

[5]Based on sample thickness of 125 mils, cured 24 hours at 25 C (77 F).

[6]Based on seven days immersion in water at 25 C (77 F).

[7]Based on sample thickness of 75 mils, cured one hour at 150 C (302 F).

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Surfaces previously in contact with any of the above materials may also cause inhibition. If in doubt, test for compatibility by brushing a small amount of catalyzed SILASTIC E RTV silicone rubber over a localized area of the surface to be reproduced. Inhibition has occurred if the rubber is gummy or uncured after the curing period has elapsed.

Inhibitors

The following materials have been checked for compatibility with

SILASTIC E RTV silicone rubber. Inhibitors include:

DOW CORNING® 3110, 3112 and 3120 RTV silicone rubbers

All GENERAL ELECTRIC®[1] RTV rubbers except 630 to 662 series

DOW CORNING® 282 adhesive

MARBLEX®[2] clay

Polysulfide MIL-S-8516

Epoxy – amine cured

SCOTCH®[3] cellophane tape

PERMACEL®[4] masking tape

Neoprene rubber

Buna N rubber

Natural rubber

Polyvinylchloride – plasticized

THERMOSET®[5] epoxy 619 with 619 hardener

THERMOSET®[5] epoxy 200 with El 869 hardener

MARASET®[6] epoxy 656 with 656 hardener

SHERWIN-WILLIAMS®[7] oil stain

Laminac polyester resin

Noninhibitors

The following materials have been checked for compatibility with SILASTIC E RTV silicone rubber. Noninhibitors include:

KINDT-COLLINS™[8] sheet and fillet wax

FREEMAN®[9] sheet and fillet wax

Permaplast X33 clay

KLEAN KLAY®[10] #20

U.S. Gypsum Hydracal

Epoxy – anhydride cured

Reapoxy-77 with hardener A

DURHAM'S ROCK HARD®[11] water putty

Vel-mix stone

POLYLITE®[12] 32-180 polyester

POLYLITE®[12] 32-112 polyester

POLYLITE®[12] 93-541 polyester

POLYLITE®[12] 34-843 polyester

SCHALK®[13] water putty

PRATT & LAMBERT®[14] spray enamel

BOYLE-MIDWAY® PLASTIC WOOD®[15]

THERMOSET®[5] epoxy 609 with 609 hardener

POLYFORM®[16] modeling clay

SHIPPING LIMITATIONS

None.

STORAGE AND SHELF LIFE

SILASTIC E RTV silicone rubber and its curing agent should be stored in closed containers at or below room temperature. The materials have a shelf life of 6 months from date of shipment from Dow Corning.

PACKAGING

SILASTIC E RTV silicone rubber is supplied with SILASTIC® E RTV curing agent in matched-lot 1.1-, 9.9-, 49.5- and 495-lb (0.5-, 4.4-, 22- and 224-kg) kits. All weights, net.

SAFE HANDLING INFORMATION

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DOW CORNING

Information About *Silastic*® J RTV Silicone Rubber

Type
Two-part silicone rubber

Physical Form
– **As supplied**
Pourable fluid
– **As cured**
Firm, flexible rubber

Cure
Heat curable at room temperature within 24 hours

Special Features
Good cut-growth resistance; high durometer hardness; low shrinkage

Primary Uses
For molds used to reproduce art objects, novelties and furniture components in urethane and other plastics; general potting and encapsulating applications

DESCRIPTION

Silastic® J RTV Silicone Rubber is a two-component, room-temperature, addition-cure silicone rubber. This product, which is part of an entire family of *Silastic* Silicone Moldmaking Rubbers, is designed for use as a flexible potting, encapsulating or moldmaking material for urethane foams and other cast plastics. *Silastic* J RTV Silicone Rubber features:

- Good cut-growth resistance
- High durometer hardness
- Low shrinkage
- Easy release

These properties help provide long mold life, highly detailed reproductions and simplified handling.

Silastic J RTV Silicone Rubber base is white and its curing agent is green to aid inspection for uniform blending. A ratio of ten parts base to one part curing agent is provided for easy mixing.

Silastic J RTV Silicone Rubber is an ideal electrical/electronic material for general potting and encapsulating of modules, relays, power suppliers, amplifiers, transformers and connectors.

HOW TO USE

Pattern Preparation

Certain contaminants sometimes used in moldmaking operations can prevent *Silastic* J RTV Silicone Rubber from curing. Patterns to be molded should be thoroughly cleaned to remove grease, oil and other surface contaminants. Care should also be taken to ensure that corners, crevices and draws are free from dirt or particles of foreign matter. A light "blow over" with compressed air is advised when the pattern has convoluted draws or undercuts.

Then the original model or pattern should be placed in a light frame of cardboard, foil, wood or other material. There should be approximately 1/4-inch clearances on all sides and over the top of the pattern. The pattern should be attached securely to the bottom of the frame so it does not float.

A pattern release agent should then be wiped or sprayed on the pattern. A light coat of release agent on the sides and underside of the top of the frame will facilitate release.

Addition of Curing Agent

Automatic mixing equipment handles *Silastic* J RTV Silicone Rubber efficiently. The product is deaired before shipment when packaged in drums.

Silastic J RTV Silicone Rubber curing agent should be mixed into the base material just before use (with either manual or mechanical stirring) in the amounts of ten parts base to one part curing agent by weight. For best curing results, use metal cans, clean glassware, or unwaxed paper containers when mixing the base and curing agent. Inclusion of air may be removed by applying a vacuum of 28 to 29 inches of mercury. Under such a vacuum, the material will expand to three to four times its original volume. As the froth collapses, the mixture will recede to its original volume. The vacuum should be held one or two minutes longer before releasing.

Pressure casting may be substituted with equal success.

Working Time

Silastic J RTV Silicone Rubber remains a flowable, pourable material for two hours after the curing agent is added.

Curing

The cure of *Silastic* J RTV Silicone Rubber occurs by a reaction between the base polymer and the curing agent. Polymerization requires 24 hours after the addition of the curing agent at room temperature. This material will not revert or depolymerize, even under conditions of elevated temperature and confinement. Vulcanization can be accelerated by heating the catalyzed material. However, this will increase the shrinkage from nil to 0.3 percent.

Vulcanization will not be accelerated at the center of the piece until the entire mass has reached the elevated temperature.

Inhibition of Cure

Silastic J RTV Silicone Rubber is formulated to have greater resistance to inhibition. However, localized inhibition of cure may be encountered at the interference when *Silastic* J RTV Silicone Rubber comes in contact with certain contaminants during the curing process. Among materials found to cause inhibition are sulfur-containing and organometallic salt-containing compounds (such as organic rubbers), and condensation cure RTV silicones.

Surfaces previously in contact with any of the above materials may also cause inhibition. If in doubt, test for compatibility by brushing a small amount of catalyzed *Silastic* J RTV Silicone Rubber over a localized area of the surface to be reproduced. Inhibition has occurred if the rubber is gummy or uncured after the curing period has elapsed.

LIMITATIONS

Not intended for medical use.

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied		
CTM[1] 0176	Appearance, base	White
	curing agent	Dark green
	Base to Curing Agent Mixing Ratio, by weight	10:1
As Catalyzed		
CTM 0176	Appearance	Green
CTM 0050	Viscosity[2] at 25°C (77°F), poise	900
CTM 0092A	Snap Time[3] at 25°C (77°F), hours	3
CTM 0092A	Cure Time[4] at 25°C (77°F), hours	24
As Cured – Physical Properties[5]		
CTM 0099	Durometer Hardness, Shore A, points	56
CTM 0137A	Tensile Strength, psi	900
CTM 0137A	Elongation, Die C, percent	250
CTM 0159A	Tear Strength, Die B, ppi	90
CTM 0022	Specific Gravity at 25°C (77°F)	1.28
CTM 0157	Linear Shrink	Nil
CTM 0137A	Tensile Strength at 150 percent Elongation, psi	610
CTM 0224	Thermal Conductivity, Cal-cm/sec-cm^2/°C	6.2×10^{-4}
CTM 0585	Linear Coefficient of Thermal Expansion, cm/cm (20-220°C)	3.1×10^{-4}
Electrical Properties[6]		
CTM 0114	Dielectric Strength, volts/mil	590
CTM 0112	Dielectric Constant at	
	100 Hz	2.94
	100 kHz	2.79
CTM 0112	Dissipation Factor at	
	100 Hz	0.0152
	100 kHz	0.0040
CTM 0249	Volume Resistivity, ohm-cm	5.15×10^{14}
CTM 0249	ARC Resistance, seconds	126

[1]CTMs (Corporate Test Methods) correspond to standard ASTM tests in most instances. Copies of CTM are available upon request.

[2]Brookfield Viscometer Model HAF, spindle #6 at 5 rpm.

[3]Time required to become nonflowable.

[4]Based on sample mass of one cubic inch.

[5]Based on sample thickness of 125 mils, cured 24 hours at 25°C (77°F).

[6]Based on sample thickness of 75 mils, cured one hour at 150°C (302°F).

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Silastic J RTV Silicone Rubber is supplied with *Silastic* J RTV Curing Agent in matched-lot 1.1-, 9.9-, 49.5- and 495-lb (0.5-, 4.4-, 22- and 224-kg) kits. All weights are net.

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DOW CORNING

Dow Corning Corporation
Midland, Michigan 48686-0994

Information About *Silastic*® M RTV Silicone Rubber

Type
Two-part silicone rubber

Physical Form
– **As Supplied**
Pourable fluid
– **As Cured**
Firm, flexible rubber

Cure
At room temperature within 16 hours or heat curable

Special Features
High inhibition resistance; formulated to work with both rigid and foam polyurethanes; good cut-growth resistance; high durometer hardness; low shrink

Primary Uses
Prototyping, architectural, furniture components

DESCRIPTION

Silastic® M RTV Silicone Rubber is a two-part, flexible moldmaking material designed especially for use with urethane foams and other casting plastics. This high-strength, tear-resistant product cures at room or elevated temperatures by an addition reaction.

The special features of *Silastic* M RTV Silicone Rubber help provide long mold life, highly detailed reproductions, and simplified handling.

Silastic M RTV Silicone Rubber base is white, and its curing agent is regal blue to aid inspection for uniform blending. An easy to mix ratio of 10:1 base to curing agent helps ensure accurate measuring and blending by hand or machine. The material cures in unlimited thickness, regardless of part configuration or degree of confinement.

HOW TO USE

Pattern Preparation

Certain contaminants used in moldmaking operations can prevent *Silastic* M RTV Silicone Rubber from curing. Patterns to be molded should be thoroughly cleaned to remove grease, oil, and other surface contaminants. Care should also be taken to ensure that corners, crevices, and draws are free of dirt or particles of foreign matter. A light "blow over" with compressed air is advised when the pattern has convoluted draws or undercuts. Then, the original model or pattern should be placed in a light frame of cardboard, foil, wood, or other material. There should be approximately 3/8-inch clearance on all sides and over the top of the pattern. The pattern should be attached securely to the bottom of the frame so it does not float.

A pattern release agent should then be wiped or sprayed on the pattern. Spreading a light coat of release agent on the sides and underside of the top of the frame will facilitate release.

A good pattern release agent can be made by combining five percent petroleum jelly and 95 percent solvent. Combine the materials and let stand overnight – then shake by hand to provide a good mix.

Addition of Curing Agent

Automatic mixing equipment handles *Silastic* M RTV Silicone Rubber efficiently. The product is deaired before shipment when packaged in drums.

Silastic M RTV Silicone Rubber curing agent should be mixed into the base material just before use (with either manual or mechanical stirring) in the amounts of ten parts base to one part curing agent by weight. For the best curing results, use metal cans, clean glassware, or unwaxed paper containers for mixing the base and curing agent. Inclusion of air during mixing may cause voids in the finished mold. Entrapped air may be removed by applying a vacuum of 28 to 29 inches of mercury. Under such a vacuum, the material will expand to three to four times its original volume. As the froth collapses, the mixture will recede to its original volume. The vacuum should be held one or two minutes longer before releasing.

Pressure casting may be substituted with equal success.

Working Time

Silastic M RTV Silicone Rubber remains a flowable, pourable material for 1 1/2 hours after the curing agent is added.

Curing

The cure of *Silastic* M RTV Silicone Rubber occurs by a reaction between the base polymer and the curing agent. Polymerization requires 24 hours after the addition of the curing agent at room temperature. This material will not revert or depolymerize, even under conditions of elevated temperature and confinement. Vulcanization can be accelerated by heating the catalyzed material. However, this will increase the shrinkage from nil to 0.3 percent. A part 1/4-inch thick will set up within 30 minutes if the temperature is maintained at 150°F (65°C). The rate at which thicker sections will set up depends on the size and shape of the piece.

Vulcanization will not be accelerated at the center of the piece until the entire mass has reached the elevated temperature. Average set-up times at various temperatures for 1/4-inch moldings are as follows:

Temperature	Demold Time
77°F (25°C)	16 hours
125°F (52°C)	60 minutes
150°F (65°C)	30 minutes
200°F (93°C)	15 minutes
250°F (121°C)	7 minutes
300°F (149°C)	5 minutes

Inhibition of Cure

Silastic M RTV Silicone Rubber is formulated to have greater resistance to inhibition. However, localized inhibition of cure may be encountered at the interface when *Silastic* M RTV Silicone Rubber comes in contact with certain contaminants during the curing process. Among materials found to cause inhibition are sulfur-containing and organometallic salt-containing compounds (such as organic rubbers), and condensation cure RTV silicones.

Surfaces previously in contact with any of the above materials may also cause inhibition. If in doubt, test for compatibility by brushing a small amount of catalyzed *Silastic* M RTV Silicone Rubber over a localized area of the surface to be reproduced. Inhibition has occurred if the rubber is gummy or uncured after the curing period has elapsed.

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied	
Appearance, Base	White
Curing Agent	Regal Blue
Base to Curing Agent Mixing Ratio, by weight	10:1
Base Viscosity at 77°F (25°C), poise	1300
As Catalyzed	
Appearance	Regal Blue
Viscosity[1] at 77°F (25°C), poise	900
Cure Time[2] at 77°F (25°C), hours	16
As Cured[3]	
Durometer Hardness, Shore A, points	59
Tensile Strength, psi	650
Elongation, Die C, percent	250
Tear Strength, Die B, ppi	90
Specific Gravity at 77°F (25°C)	1.29
Linear Shrink	Nil

[1]Brookfield Viscometer Model HAF, spindle #6 at 5 rpm.

[2]Based on sample mass of one cubic inch.

[3]Based on sample thickness of 125 mils, cured 24 hours at 77°F (25°C).

Specification Writers: Please obtain a copy of the Dow Corning Sales Specification for this product and use it as a basis for your specifications. It may be obtained from any Dow Corning Sales Office, or from Dow Corning Customer Service in Midland, MI. Call (517) 496-6000.

LIMITATIONS

Not intended for medical use.

STORAGE AND SHELF LIFE

Silastic M RTV Silicone Rubber base and curing agent should be stored in closed containers at or below room temperature. The materials have a shelf life of six months from date of shipment.

PACKAGING

Silastic M RTV Silicone Rubber base is supplied with *Silastic* M RTV Silicone Rubber curing agent in matched lot, 1.1-, 9.9-, 49.5-, and 495-lb (0.5-, 4.4-, 22-, and 224-kg) kits. All weights net.

SAFE HANDLING INFORMATION
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DOW CORNING

Dow Corning Corporation
Midland, Michigan 48686-0994

Information About High Technology Silicone Materials

DOW CORNING

DESCRIPTION

Encapsulants

DOW CORNING® 3110, 3112 and 3120 RTV rubbers are pourable rubber bases that become firm, flexible silicone rubber when cured. They can be pigmented for color coding* and cured with any of four catalysts. The cured rubbers exhibit good dielectric properties, and various combinations of base and catalyst allow a wide range of working times and curing rates that satisfy essentially all potting, coating and moldmaking needs.

These RTV rubbers:

- Are easily mixed and poured, without preheating
- Cure at room temperature
- Cure in any thickness without exothermic heat
- Shrink little during cure; produce minimum stress on components
- Give accurate reproduction of masters for moldmaking
- With primer, can be bonded to metal, glass, silicone and organic resin laminates or moldings, and to vulcanized silicone rubber
- Provide wide service temperature ranges
- Protect components from moisture, dirt, corona, weathering and corrosive atmospheres
- Absorb mechanical shock and vibration
- Are easy to repair by cutting away old material and repouring fresh encapsulant

*Except DOW CORNING 3120 RTV rubber which is red as supplied.

DOW CORNING® 3110, 3112, AND 3120 RTV RUBBERS

Type	Two-part RTV silicone rubber
Color	
DOW CORNING 3110 and 3112 RTV rubbers	White
DOW CORNING 3120 RTV rubber	Red
Physical Form	
as supplied	Pourable liquid
as cured	Firm, flexible silicone rubber
Cure	At room temperature; choice of four catalysts offers cure times ranging from 12 minutes to 24 hours
Primary Uses	Potting and encapsulating of electrical/electronic products; moldmaking RTV rubbers

Catalysts

The paste catalysts consist of active catalysts plus filler and silicone polymer. A 10:1 recommended mixing ratio assures more accurate measuring and mixing of catalyst, particularly when automatic equipment is used to mix and/or dispense the RTV silicone rubber.** Do not use DOW CORNING® RTV catalysts S or F when molding polyesters because they will be inhibited. DOW CORNING® RTV catalysts 1 and 4 do not have corrosion inhibitors.

**A 10:1 mixing ratio is not recommended for DOW CORNING RTV catalyst 4.

TABLE I: CATALYSTS

Catalyst	Color	Consistency	Cure Time	Cure Conditions
F (fast rate)	light tan	paste	12 min-5 hrs	room temperature – any thickness or in confined spaces
S (standard rate)	light blue	paste	5-12 hrs	same as F
1 (same as S but no corrosion inhibitor)				
4 (fast rate, 100:1 ratio)	clear straw	liquid	20 min-2 1/2 hrs	same as F

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

		DOW CORNING 3110 RTV rubber[1]	DOW CORNING 3112 RTV rubber[1]	DOW CORNING 3120 RTV rubber[1]
Processing Considerations				
	Color	White[2]	White[2]	Red
	Deep Section Cure, 1" depth in metal can	Yes	Yes	Yes
	Recommended Primer	1201[3]	1201[3]	1201[3]
ASTM D 1084B	Viscosity at 25 C (77 F), poises	140	350	250
ASTM D 792A	Specific Gravity at 25 C (77 F)	1.17	1.35	1.47
MIL-S-23586	Corrosion Resistance	Good/Pass[4]	Good/Pass[4]	Good/Pass[4]
Physical and Chemical Properties				
	Radiation Resistance, Cobalt 60 Source, 25 C (77 F), megarads	100	100	100
ASTM D 570	Water Absorption, 7 days at 25 C (77 F), percent	0.4	0.2	0.2
	Useful Temperature Range, degrees	-55 to 200 C (-67 to 392 F)	-55 to 250 C (-67 to 482 F)	-55 to 300 C (-67 to 572 F)
ASTM D 2214	Thermal Conductivity, Cenco-Fitch, 25-200 C (77-212 F), gm cal/cm² sec-(degrees C/cm)	5.0×10^{-4}	6.0×10^{-4}	7.7×10^{-4}
MIL-1-16923C	Thermal Shock, 10 cycles	Pass	Pass	Pass
	Weight Loss, 96 hrs/200 C (392 F), percent	6	3.7	5.7
	Volume Expansion, 25-150 C (77-302 F), cc/cc/degrees C	7.5×10^{-4}	5.0×10^{-4}	5.2×10^{-4}
	Specific Heat, cal/gm/C	0.35	0.33	0.32
ASTM D 746	Brittle Point, degrees	-100 C (-143 F)	—	-100 C (-143 F)
	Fire Resistance	Self-extinguishing	Self-extinguishing	Self-extinguishing
Mechanical Properties				
ASTM D 412	Tensile Strength, die C psi	350	650	650
ASTM D 412	Elongation, die C percent	200	150	100
ASTM D 2240	Durometer Hardness, Shore A	45	60	60
	Linear Shrinkage, 3 days at 25 C (77 F), percent	0.4	0.4	0.3
Electrical Properties				
ASTM D 495	Arc Resistance, seconds	90	125	125
ASTM D 150	Dielectric Constant, at 25 C (77 F)			
	100 Hz	3.00	3.20	3.80
	1 KHz	—	—	3.80
	1 MHz	2.90	3.10	3.70
	1 GHz	2.89	2.95	3.50
ASTM D 150	Dissipation Factor, at 25 C (77 F)			
	100 Hz	0.012	0.030	0.030
	1 KHz	0.010	0.015	0.020
	1 MHz	0.0003	0.005	0.005
	1 GHz	0.006	0.005	0.004
ASTM D 149	Dielectric Strength, 1/16" sample, volts/mil	500	500	500
ASTM D 257	Volume Resistivity, 500 V dc, ohm-cm	1.0×10^{13}	1.0×10^{13}	5×10^{13}

[1] Using DOW CORNING RTV catalyst F or S at 10:1 base to catalyst ratio. Wide departures from normal 10:1 ratio may slightly alter physical properties such as hardness and elongation.

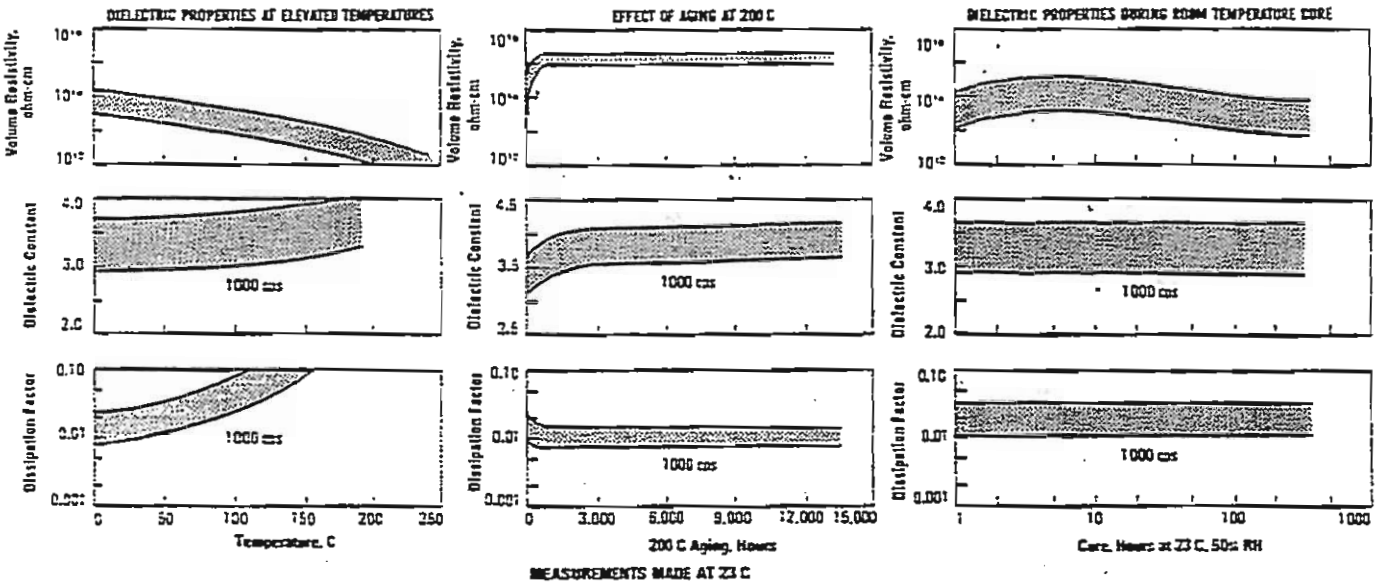
[2] Can be pigmented for color coding.

[3] DOW CORNING® 1201 RTV primer.

[4] With DOW CORNING RTV catalysts S and F.

Specification Writers: Please contact Dow Corning Corporation, Midland, Michigan, before writing specifications on these products.

TABLE II: TYPICAL ELECTRICAL PROPERTIES OF DOW CORNING RTV RUBBERS



HOW TO USE

Preparation of Units

DOW CORNING RTV rubbers will bond to metals, glass, silicone and organic resin laminates or moldings, or to vulcanized silicone rubber. To insure maximum reliability and complete environmental protection, the following procedure should be followed:

1. Clean assembly of all contaminants such as oil, grease, solder flux, moisture and dirt. Suitable cleaning solvents include toluene, xylene, acetone and fluorocarbon solvents. Ultrasonic cleaning is most effective. *Caution: When using solvents, provide adequate ventilation. Follow all precautions given on solvent container label.*

2. Dip, spray or brush surfaces with DOW CORNING 1201 RTV primer and allow to air-dry. All solvent must be removed before potting. Silicone rubber surfaces should not be primed, but should be cleaned and abraded.

Catalyst Selection

DOW CORNING RTV catalysts F, S and 1 are paste catalysts consisting of an organometallic compound and inert fillers in a silicone polymer. The most frequently used catalyst concentration is 10 percent by weight of the RTV base. Varying the catalyst concentration will change the curing rate as indicated in Table III, "Room Temperature Curing Rate vs. Catalyst Concentration."

DOW CORNING RTV catalyst 4 is used where fast curing is necessary for polyester molds. The recommended mixing ratio is 100:1.

DOW CORNING RTV catalyst F contains stannous octoate* as its active ingredient, and is used for high speed production.

It is ideally suited for use with automated mixing-dispensing equipment, where the mixing is done in a mixing head immediately before dispensing. Working time with 10 percent of this catalyst is about 1 to 2 minutes. DOW CORNING RTV catalyst F will lose its activity rapidly when exposed to air. Keep catalyst containers tightly closed when not in use.

When using DOW CORNING RTV catalyst F in concentrations less that 10 percent, incomplete cure may result on surfaces exposed to air. Confined materials cure well at low catalyst concentrations.

DOW CORNING RTV catalysts S and 1 contain dibutyl tin dilaurate** as their active ingredient. These are widely used catalysts because they permit about 30 minutes working time.

CAUTION

Upon contact, DOW CORNING catalysts F and 4 will irritate skin and eyes. DOW CORNING catalysts S and 1 will burn skin and eyes. In case of eye contact, flush with water. Seek prompt medical attention. Skin contact areas should be thoroughly washed with soap and water. Persistent irritation should receive medical attention.

Adjusting Viscosity

These rubbers can be made more pourable by adding DOW CORNING® 200 fluid (20 cs) to the compound just prior to catalyst addition.

Addition of silicone fluid thinner will extend pot life and curing time of RTV rubbers. Five percent thinner, for example, will extend the pot life by about 30 percent and the cure time by about 10 percent.

Ten percent DOW CORNING 200 fluid greatly reduces the viscosity of the

*Available in concentrated form as "Nuocure 28" from Tenneco Chemicals, Inc. Intermediates Division, Piscataway, New Jersey.

**Available in concentrated form as "Thermolite-12" from M & T Chemicals Corporation, Rathway, New Jersey.

TABLE III: ROOM TEMPERATURE CURING RATE vs CATALYST CONCENTRATION

DOW CORNING 3110 RTV rubber	*Working Time*[1]	*Pot Life*[2]	*Cure Time*[3]
15% Catalyst F	1 min	10 min	1 1/2 hrs
10% Catalyst F	1 min	25 min	2 hrs
5% Catalyst F	13 min	65 min	4 1/2 hrs
15% Catalyst S	35 min	2 hrs	5 1/2 hrs
10% Catalyst S	50 min	2 1/2 hrs	6 1/2 hrs
5% Catalyst S	80 min	4 1/2 hrs	8 1/2 hrs

DOW CORNING 3112 RTV rubber	*Working Time*[1]	*Pot Life*[2]	*Cure Time*[3]
15% Catalyst F	1 min	30 min	2 hrs
10% Catalyst F	1 min	1 hr	5 hrs
15% Catalyst S	40 min	2 1/2 hrs	5 1/2 hrs
10% Catalyst S	45 min	3 hrs	6 hrs
5% Catalyst S	80 min	5 1/2 hrs	7 hrs

[1]Working time is the elapsed time from catalyst addition to the time when the mixture has tripled its initial catalyzed viscosity. [Measured at 25 C (77 F)].

[2]Pot life is the time required for the catalyzed mixture to cease being a fluid. It is measured by depressing the tip of a 0.25-inch micro spatula below the surface of the mixture and withdrawing it. When the string of material attached to the spatula snaps before being withdrawn one inch, the end of the pot life has been reached. [Measured at 25 C (77 F)].

[3]Cure time is the time for the catalyzed encapsulant to reach one-half of its nominal hardness. [Cured at 25 C (77 F)].

compound and is the maximum recommended. At this concentration only small changes in physical properties are measured. Large amounts of fluid, however, can lower the physical properties of the cured encapsulant. Electrical properties are not adversely affected, but thermal endurance may be decreased.

Mixing

DOW CORNING 3110, 3112 and 3120 RTV rubbers, with DOW CORNING RTV catalysts F, S or 1, have been designed specifically for use with automatic mixing and dispensing equipment.

DOW CORNING 3110 RTV rubber should be stirred before using, since filler separation may occur upon prolonged standing.

Catalysts can be added to the base material in its shipping container or any clean, dry container. If vacuum deairing is planned, the container should be no more than one-half full to allow for the expansion during the vacuum cycle.

Either hand mixing or mechanical mixing is satisfactory. With either method, care should be taken not to whip large amounts of air into the mixture. Avoid vigorous mechanical mixing since sufficient frictional heat may be generated to accelerate the cure rate.

Vacuum deairing may not be necessary, particularly with DOW CORNING 3110 RTV rubber. When it is necessary, it should be done first in the mixing container. A vacuum of at least 29 inches of mercury should be held until most bubbling has ceased. For best results, the mixture should be vacuum dealred again after it has been poured in place, especially when densely packed circuit components are being potted. For impregnation of units such as coils or transformers, the vacuum cycle can be followed by the application of 10 to 50 psi air pressure.

Extending Pot Life

The pot life of DOW CORNING RTV rubbers catalyzed with 10 percent DOW CORNING RTV catalysts S and 1 can be extended by refrigeration as follows:

Temperature, degrees	*Pot Life, hrs*
37 C (98 F)	1-2
25 C (77 F)	2-4
5 C (41 F)	6-10
-2 C (-13 F)	24-100

Applying

In potting with DOW CORNING RTV rubbers, the part or assembly to be packaged is placed in a form with clearance at all points where sealing is necessary. This form may be made of paper, aluminum foil, metal or plastic. For release agent, a three percent detergent solution in water is normally satisfactory. This release agent is applied to the form and allowed to dry. DOW CORNING RTV rubbers are then poured into the forms.

For fast and complete filling, a low-viscosity rubber such as DOW CORNING 3110 RTV rubber is recommended.

Where printed circuit boards and similar assemblies are to be dip coated, select the viscosity grade that will give the desired coating thickness. To apply DOW CORNING RTV rubbers as conformal coatings, immerse parts in the catalyzed compound, withdraw them slowly, pausing just before the part leaves the dip tank to minimize stringing, and hang on a rack to cure. Allow one to two hours between dips. Two dips in a low-viscosity-grade encapsulant are suggested for optimum protection.

For maximum assurance of void-free potting, a vacuum greater than 29 inches of mercury is recommended to facilitate removal of air.

Color Coding

DOW CORNING 3110 and 3112 RTV rubbers can be readily color coded by

mixing in masterbatch pigments. These should be mixed into the base material in proper proportion just prior to adding catalyst.

Fourteen different colors, available from the Ferro Corporation, have been tested and found to have little or no effect on the properties of DOW CORNING RTV rubbers when used in a concentration of three percent by weight. The manufacturer's designation for these pigments are:

V-1747	Black
V-52	White
V-1721	Light Gray
V-1722	Dark Gray
V-68	Aluminum
V-53	Aluminum-Bronze
V-2876	Red
V-1232	Blue
V-2608	Green
V-1936	Yellow
V-2658	Turquoise
V-1100	Red Brown
V-1107	Brown
V-1105	Buff

Curing

The RTV rubbers should be cured at temperatures ranging from 23 to 38 C (73 to 100 F) for standard cure rates. For accelerated cure rates, all base and catalyst combinations can be heated. However, to avoid incomplete surface cure when heat accelerating DOW CORNING catalysts S and F, temperatures above 60 C (140 F) should not be used unless the compound is totally enclosed in a mold.

Curing rate is a function of temperature and humidity. Curing time will increase at temperatures below 23 C (73 F). Although the RTV rubbers are formulated to cure in dry atmospheres, as low as 20 percent relative humidity, exposure to high humidity will tend to decrease curing time.

Deep-Section Cure

DOW CORNING RTV catalysts S and 1 have been specially compounded to assure deep section curing of these rubbers.

DOW CORNING 3110, 3112, and 3120 RTV rubbers may depolymerize when overheated in total confinement. To minimize this effect, pottings which must operate in total confinement at elevated temperatures must be given a graduated post cure which allows volatiles to escape. During the graduated post cure, the temperature should be increased approximately 25 C (77 F) per hour depending upon thickness of potted section. A final bake of four hours at a temperature 50 C (122 F) degrees above the maximum operating temperature of the device is recommended.

To reduce the possibility of depolymerization, SYLGARD® silicone elastomers may be used. These products cure by an addition reaction which liberates no volatiles. For maximum assurance of stability at elevated temperatures, these Dow Corning products are recommended. They do not require post cure to achieve stable performance.

SHIPPING LIMITATIONS

None.

STORAGE AND SHELF LIFE

DOW CORNING 3110, 3112, and 3120 RTV rubbers and DOW CORNING RTV catalysts should be stored in closed containers. Shelf life of these rubbers and catalysts is 12 months from date of shipment when stored in original, unopened containers at 23 C (75 F). In all cases, these encapsulants should be stored at temperatures below 32 C (90 F).

PACKAGING

DOW CORNING RTV rubber bases are supplied in 1-, 10-, 50-, and 450-lb (.45-, 4.5-, 22.5-, and 205-kg) containers, net weight.

Catalysts are not supplied with rubber bases. They must be ordered separately. DOW CORNING RTV catalysts S and 1 are supplied in 0.1-lb (45-g) tubes and 1-, 5- and 45-lb (0.45-, 2.25- and 20.5-kg) containers, net weight. DOW CORNING RTV catalyst F is supplied in 0.1 and 3 x 1/3-lb (45- and 154-g) tubes and 45-lb (20.5-kg) containers, net weight. DOW CORNING RTV catalyst 4 is supplied in 0.01- and 0.1-lb (4.5- and 45-g) tubes, net weight.

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Information About HS II RTV High Strength Moldmaking Silicone Rubber Product Line

DOW CORNING

DESCRIPTION

DOW CORNING® HS II RTV high strength moldmaking silicone rubber is a two-part, medium-viscosity silicone rubber.

The DOW CORNING® HS II RTV high strength moldmaking silicone rubber product line features DOW CORNING HS II RTV high strength moldmaking silicone rubber with three separate and unique catalysts and a special thixotropic additive:

- DOW CORNING® HS II 20-1 clear catalyst: highest tear, low mixed viscosity
- DOW CORNING® HS II 10-1 colored catalyst: lowest durometer, pink dye aids inspection for uniform blending and avoids pigment settling problems
- DOW CORNING® HS II 10-1 clay catalyst: excellent for curing against both ROMA™[1] plastilina and CHAVANT™[2] plastelina clays; green pigment aids inspection for uniform blending
- DOW CORNING® HS II thixotropic additive: a liquid additive that, when mixed with catalyzed DOW CORNING HS II RTV high strength moldmaking silicone rubber, converts the mixture to a nonflowable paste ideal for producing skin molds, preferred for economic reasons or when a mold is required of a vertical object that cannot be removed from its position

Benefits of the DOW CORNING HS II RTV high strength moldmaking silicone rubber product line include:

- Excellent detail reproduction
- Exceptional release characteristics
- Low mixed viscosity (easier to deair)
- Low shrinkage
- Excellent tear strength
- No exotherm on cure
- Cure not sensitive to inhibition

DOW CORNING® HS II RTV HIGH STRENGTH MOLDMAKING SILICONE RUBBER PRODUCT LINE

Type	Medium-viscosity, two-part elastomer
Physical Form	Pourable liquid
Special Properties	Very high tear strength and elongation; excellent mold release
Special Features	Three unique catalysts and a special thixotropic additive
Primary Uses	High-strength, flexible silicone rubber molds; fabrication of parts

HOW TO USE – GENERAL

To ensure maximum reliability and performance, the following information should be read carefully.

Preparation

The original from which the mold is to be made should be thoroughly cleaned to remove dirt and all contaminants. When a solvent is used, care should be taken to ensure that it is compatible with the original, and sufficient time should be allowed for the solvent to evaporate fully. If required, the original and the holding box should be coated with a release agent. This is particularly important with porous substrates. Suitable release agents are solvent solutions of petroleum jelly or aqueous soap solutions.

When the original is a sulfur-containing clay, DOW CORNING HS II 10-1 clay catalyst is recommended. When casting DOW CORNING HS II RTV high strength moldmaking silicone rubber with DOW CORNING HS II 10-1 clay catalyst in thick section (1/4-inch thickness or greater) against sulfur-containing clays such as ROMA plastelina or CHAVANT plastelina clays, no surface treatment is required. However, when casting in thin sections (less than 1/4-inch in thickness), ROMA plastelina clays #1 and #2 may require minimal surface treatment.

Mixing

DOW CORNING HS II catalyst should be mixed into the base material just before use (with either manual or mechanical stirring). It is always good practice to stir/shake both the base and the catalyst prior to use. This is especially true with DOW CORNING HS II 10-1 clay catalyst to ensure suspension of the pigment.

Mixing should be complete within 2 minutes and the temperature should not exceed 35 C (95 F). Hand mixing is satisfactory, but care should be taken to avoid entrapping too much air or splashing the catalyst.

[1]"Roma" is a trademark of Sculpture House, Inc.
[2]"Chavant" is a trademark of Chavant, Inc.

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TYPICAL PROPERTIES

These values are not intended for use in preparing specifications.

As Supplied – HS II Base	
Color	White
Specific Gravity	1.21
Nonvolatile Content, percent	98
Viscosity, cps	36,200

	20:1 Clear Catalyst	*10:1 Colored Catalyst*	*10:1 Clay Catalyst*
As Supplied			
Color	Clear	Pink	Green
Viscosity, cps	30	50	50
As Catalyzed			
Specific Gravity	1.21	1.19	1.20
Viscosity, cps	24,000	24,000	25,000
Working Time, approximate hours	2	1.5	0.75
As Cured – 7 Days at Room Temperature 25 C (77 F)			
Durometer Hardness, Shore A	20	16	25
Tensile Strength, psi	600	600	560
Elongation, percent	500	470	340
Tear Strength, die B, ppi	140	135	120
Circle Shrink, percent			
after 24 hours at 25 C (77 F)	0.20	0.26	0.21
after 7 days at 25 C (77 F)	0.30	0.48	0.40

Specification Writers: Please obtain a copy of the Dow Corning Sales Specification for this product, and use it as a basis for your specifications. It may be obtained from any Dow Corning Sales Office, or from Dow Corning Product Information in Midland, MI. Call (517) 496-6000.

Deairing

To ensure void-free molds and to obtain the maximum pot life, it is important that the catalyzed mixture is deaired prior to use.

Deair the mixture under a vacuum of 26 to 29 inches of mercury and hold until it completely expands and recedes to the original level (3 to 5 minutes maximum).

CAUTION: Deairing for more than 3 to 5 minutes can cause a slower cure and deep section cure problems. The container should have at least 5 times the mixture volume to allow for the expansion.

Pouring the Mixture

Depending on catalyst selection, the catalyzed mixture has a working time* of 45 minutes to 2 hours under normal working temperatures. It should be poured carefully to avoid entrapping air and should be allowed to flow from one corner of the mold to fill the required volume. DO NOT SCRAPE the sides of the container holding the catalyzed mixture.

Cure

The catalyzed mixture will cure to a flexible rubber within 24 hours, after which it can be demolded. Optimum mechanical properties are developed within 7 days.

The cure rate can be accelerated with heat but the temperature cannot exceed 43.3 C (110 F). Optimum properties are not achieved by varying the base to catalyst mixing ratio from the recommended ratios.

HOW TO USE – THIXOTROPIC ADDITIVE

The substrate from which a mold will be made should first be cleaned, and, if necessary, coated with a release agent (petroleum jelly, PTFE spray, or soap solution are suitable). This is particularly important for porous substrates.

The substrate should then be coated with a thin precoat (print coat) of catalyzed DOW CORNING HS II RTV high strength moldmaking silicone rubber and DOW CORNING HS II 10-1 clay catalyst (100 parts base plus 10 parts catalyst). Once the print coat has started to cure, a second coat may be applied. These coatings can be applied by either brushing or spraying. To ensure a void-free coating, the mixture should be deaired prior to use.

Once this layer has started to cure, but is still tacky, the thixotropic mixture should be prepared by thoroughly mixing together DOW CORNING HS II RTV high strength moldmaking silicone rubber base, DOW CORNING HS II 10-1 clay catalyst and DOW CORNING HS II thixotropic moldmaking additive in the ratio of 100:10:1 (base:catalyst:additive) parts by weight. It is not necessary to deair this mixture.

This mixture should be applied over the precoat with a spatula. The addition of a pigment to the thixotropic mixture aids in identifying the areas to be coated. Suitable pigments can be obtained from the Ferro Corporation, 1301 N. Flora Street, Plymouth, Indiana 46563, (210) 936-5131.

The pigments are used at a level of 0.5 part by weight. If necessary, more than one layer of the thixotropic additive can be applied to achieve a thick coating. To ensure optimum adhesion between the layers, the next layer should be applied before the previous one has fully cured and is still tacky.

Full cure is achieved within 24 hours, after which demolding can take place. For large or complicated molds, it is recommended to back the silicone mold with plaster or polyester prior to removal.

HANDLING PRECAUTIONS

With DOW CORNING HS II RTV high strength moldmaking silicone rubber base, direct eye contact may cause temporary discomfort. Otherwise, DOW CORNING HS II RTV high strength moldmaking silicone rubber base is nonhazardous and nonflammable. DOW CORNING HS II RTV high strength moldmaking silicone rubber catalysts are eye and skin irritants, and their vapors may be harmful. They are also flammable (flash point 29.4 C [85 F]), so appropriate precautions must be taken.

*Time when catalyzed mixture becomes nonflowable (usually tripling the initial viscosity).

TYPICAL PROPERTIES – DOW CORNING HS II RTV THIXOTROPIC ADDITIVE
These values are not intended for use in preparing specifications.

As Supplied	
Appearance	Off-white, translucent liquid
Viscosity, cps	350
Specific Gravity	1.04
As Mixed[1] With Catalyzed DOW CORNING HS II RTV High Strength Moldmaking Silicone Rubber[2]	
Working Time, minutes	45
Cure Time, hours	24
Slump on Cure, 8-mm thick coating, mm	4

[1]Recommended mixing ratio is 100:10:1 (base:catalyst:additive), by weight.

[2]The mechanical properties are similar to DOW CORNING HS II RTV high strength moldmaking silicone rubber.

Specification Writers: Please obtain a copy of the Dow Corning Sales Specification for this product, and use it as a basis for your specifications. It may be obtained from any Dow Corning Sales Office, or from Dow Corning Product Information in Midland, MI. Call (517) 496-6000.

DOW CORNING HS II RTV thixotropic moldmaking additive is noncorrosive and should present no health or safety hazard when used as recommended.

Safe handling instruction sheets for DOW CORNING HS II RTV high strength moldmaking silicone rubber base and catalysts are available from your nearest Dow Corning sales office.

STORAGE AND SHELF LIFE

When stored in original, unopened containers at 25 C (77 F), DOW CORNING HS II RTV high strength moldmaking silicone rubber base and catalysts have a shelf life of 6 months from date of shipment.

When stored in closed containers at 25 C (77 F), DOW CORNING HS II RTV thixotropic moldmaking additive has a shelf life of 12 months. When stored below 20 C (68 F), it may solidify. The product can be readily reliquified by the application of heat.

Base and catalysts are moisture sensitive. Care should be taken to ensure that containers are tightly closed after use.

PACKAGING

DOW CORNING HS II RTV high strength moldmaking silicone rubber is sold separately from the catalysts. The base is packaged in 9-, 45- and 440-lb (4.1-, 20.4- and 199.6-kg) containers. DOW CORNING HS II 20-1 clear catalyst is packaged in 0.45-, 2.25- and 22-lb (203-g, 1- and 10-kg) containers. DOW CORNING HS II 10-1 colored catalyst and DOW CORNING HS II 10-1 clay catalyst are packaged in 0.9-, 4.5- and 44-lb (408-g, 2- and 20-kg) containers. A 1.05-lb (477-g) kit with base and DOW CORNING HS II 20-1 clear catalyst and a 1.1-lb (0.5-kg) kit with base and DOW CORNING HS II 10-1 colored catalyst are also offered.

DOW CORNING HS II RTV thixotropic additive is available in a 1-lb (454-g) container.

MSDS INFORMATION

ATTENTION: PRODUCT SAFETY INFORMATION REQUIRED FOR SAFE USE IS NOT INCLUDED. BEFORE HANDLING, READ PRODUCT AND MATERIAL SAFETY DATA SHEETS AND CONTAINER LABELS FOR SAFE USE, PHYSICAL AND HEALTH HAZARD INFORMATION. THE MATERIAL SAFETY DATA SHEET IS AVAILABLE FROM YOUR DOW CORNING REPRESENTATIVE, OR DISTRIBUTOR, OR BY WRITING TO DOW CORNING CUSTOMER SERVICE, OR BY CALLING (517) 496-6000.

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DOW CORNING

DOW CORNING

Tips for successful moldmaking

Once you've selected the correct product and determined how to use it properly, you're on the way to making good, flexible molds with silicone rubber. The following recommendations will further ensure your success.

1. De-airing

De-airing is recommended for all silicone moldmaking rubbers when not using automatic dispensing equipment. The small air bubbles that result from hand mixing become trapped in the mixture and, if not removed by de-airing, can interfere with exact surface reproduction. One exception is DOW CORNING® 3110 RTV silicone rubber. Due to its low viscosity, this material can be used in many applications without de-airing.

Because the mixture of base and catalyst or base and curing agent will expand during de-airing, it is important to use a container that is between three to five times the volume of the material itself. The higher viscosity silicone moldmaking rubbers will expand the most.

The mixture can be quickly and easily de-aired in a vacuum chamber. This important step usually takes just a few minutes. Entrapped air may be removed by applying a vacuum of 28 to 29 inches of mercury. The material will expand and then recede to its original level. For approximate time to complete de-airing, consult the individual product data sheets.

2. Inhibition

Cure of Dow Corning RTV materials may be inhibited by certain contaminants in or on the pattern to be molded. The inhibition reaction will impair or stop the crosslinking necessary for the RTV material to cure, resulting in tackiness at the pattern interface or a total lack of cure throughout the mold.

If in doubt as to possible surface inhibition, a "patch test" is recommended. Brush or pour a small amount of the catalyzed RTV selected onto a non-critical area of the pattern. Inhibition has occurred if the rubber is gummy or uncured after the recommended cure time has passed.

Addition Cure Systems. Inhibition in addition cure systems (platinum cure) such as the SILASTIC® silicone moldmaking product line can range from tackiness to complete lack of cure. Among materials found to cause inhibition are sulfur-containing modeling clays, natural rubber such as latex and rubber gloves, masking tape, amine or sulfur-containing materials, and condensation cure (tin catalyzed) silicone RTVs.

Surfaces previously in contact with any of the materials mentioned may also be inhibited. Water, when present on the part to be molded, can also cause inhibition.

Condensation Cure Systems. Inhibition in condensation cure systems (tin catalyzed) such as DOW CORNING® 3100 series and DOW CORNING® HS series RTV silicone rubbers is not common. However, there are some sulfur-containing modeling clays that can retard the cure of some of the condensation cured RTVs. Complete cure may take days (with severe inhibition), but unlike inhibited addition cure materials, the condensation cure RTVs will cure when the clays are removed.

In the DOW CORNING HS series, DOW CORNING® HS II 10-1 clear and 10-1 clay catalyst and DOW CORNING® HS-III 10-1 clear and 10-1 clay catalysts, when used with their respective bases, have been formulated to cure against inhibition-prone clays.

Molding clays and tapes that are compatible with all silicone moldmaking rubbers from Dow Corning can be found in "Suppliers of Moldmaking Equipment and Materials" available in "LITGUIDE."

Techniques to Prevent Inhibition. A standard practice to prevent inhibition is the use of a "barrier coating" to prevent the inhibiting agent from contacting the uncured RTV material. A thin layer of clear acrylic lacquer such as KRYLON®[1] Crystal Clear Acrylic Spray Coating sprayed directly onto the pattern is an effective barrier coating in most instances.

[1] "KRYLON" is a registered trademark of Borden, Inc.

Polyvinyl alcohol (PVA) is another effective barrier coat. This water-based solution can be applied by brushing, wiping, or spraying onto the master. It is important the film be completely dry before molding.

After the mold is cast, the film of PVA can be removed from the pattern by placing it underwater and rubbing briskly. The film will redissolve.

3. Thinners

DOW CORNING 200® Silicone Fluid serves as a thinner and can be used with all Dow Corning silicone moldmaking rubbers. A wide variety of viscosities are available; however, 20, 50, 100, and 350 centistokes viscosities are most commonly used.

Using a thinner to lower the viscosity of the RTV bases requires only 1 to 3% of the 200® Fluid and does not affect the physical properties of the rubber when using a thinner to reduce durometer.

4. Release Agents

<u>For Patterns/Masters</u>. A release agent should be used to ensure easy removal of the cured rubber from the pattern/master. For molds cured at room temperature, a simple mixture of 5 parts petroleum jelly to 95 parts solvent is recommended. Suitable solvents include VM&P naphtha or mineral spirits.

The petroleum jelly-solvent mixture can easily be prepared by putting the items together in a suitable container and setting aside overnight. With slight agitation before use, the mixture is ready to apply.

To ensure complete coverage, brush the mold liberally with the petroleum jelly-solvent mixture; then hit with a spray of air from an air gun. The air will aid in evaporating the solvent, eliminate puddling and the resultant loss of detail. This process will leave a thin film of petroleum jelly over the entire pattern/master.

When casting a two-part mold, it is extremely important to completely cover the cured half of the mold with a good release agent to prevent the two halves from bonding together. Straight petroleum jelly can be used, as well as a solution of 30 to 50% petroleum jelly. Dusting with talc or baby powder has been found to be effective, as well as the use of TEFLON aerosols.

<u>For Silicone Molds</u>. When first cast, silicone rubber molds exhibit natural release characteristics. Over time, however, the reactant agents in most casting resins will deplete mold lubricity and parts will begin to stick in the mold. A release agent should be used at the first sign of sticking and may reapplied when sticking reoccurs.

When using a silicone release agent, it is important to burnish in the release agent only on the area(s) where sticking occurs.

If using a silicone release agent in an aerosol container, there are cautions to be taken. Silicone can cause non-wetting spots (fisheyes) in nearby areas where painting is being performed. It is best to use straight dimethyl fluid (DOW CORNING 200® Fluid) and rub it into the mold where sticking is occurring. Wiping off any excess will prevent non-wetting areas on the piece(s) cast from the mold.

There are several types of release agents available. A listing of some of the companies that supply them can be found in the "LITGUIDE" under "Suppliers of Moldmaking Equipment and Materials."

5. Amount of Rubber Needed to Cast a Mold

- DOW CORNING® HS II RTV high strength moldmaking rubber: 20 grams/cubic inch
- DOW CORNING® HS III and HS IV RTV high strength moldmaking rubbers: 18.8 grams/cubic inch
- DOW CORNING® 3110 RTV silicone rubber: 19 grams/cubic inch
- DOW CORNING® 3112 RTV silicone rubber: 23 grams/cubic inch
- DOW CORNING® 3120 RTV silicone rubber: 25 grams/cubic inch
- SILASTIC® E and T RTV silicone rubbers: 18 grams/cubic inch
- SILASTIC® J, K, L, and M RTV silicone rubbers: 21 grams/cubic inch

6. Patching Torn Molds

Using a steel brush, abrade the area to be patched, then clean the tear with a good grease cutting solvent such as naphtha or mineral spirits. Be sure the solvent has completely evaporated before proceeding.

Because silicone rubber sticks so well to itself, for the strongest patch, it is recommended that you use the same silicone rubber that was used to make the mold. SILASTIC® 732 RTV multi-purpose sealant can also be used to repair torn molds.

7. Compression Casting

When using silicone rubber materials to do compression casting, holes must be drilled to permit venting. One hole for every 25 square inches of surface area should be sufficient. Maximum size is 1/16 inch.

8. Oak Wood Patterns

When using new oak wood patterns, a microsized porosity often occurs at the open grain of the wood. To avoid this, apply some petroleum jelly to a clean cloth and gently rub the surface in the direction of the grain.

9. Mold Box Release

A coating of DOW CORNING® 236 RTV dispersion on wooden mold boxes prevents resins, especially polyurethanes, from sticking to the mold boxes.

10. Mold Life Extension

a. Barrier Coating. The use of a barrier coat when casting polyurethanes can greatly extend mold life, in some cases up to 200 percent. The barrier coat should be sprayed into the silicone mold prior to each casting. When the cast part is removed from the mold, the barrier coat becomes the outer skin of the casting. The barrier coat can then be stained or painted, an important feature.

Note that this type of barrier coat is different than the barrier coat mentioned in "Techniques To Prevent Inhibition."

b. Reconditioning. Reconditioning can be accomplished by burnishing into the surface a low viscosity DOW CORNING 200® Fluid. When the mold is to be put back in use, any excess fluid should be removed from the surface. This is necessary to assure the cast parts will be paintable. Non-wetting or "fisheyes" can occur on the surface of the cast parts if all excess DOW CORNING 200® Fluid is not removed.

c. Bake-Out. A bake-out is recommended to remove the hardeners, plasticizers and other materials that leach out of the casting materials and are gradually absorbed into silicone molds.

A slow, gradual bake-out at 93∞C (200∞F) for eight hours or a rapid bake-out at 204∞C (400∞F) for two hours can be used.

11. Library Life

To extend the library life (shelf life) of a cured silicone rubber mold, it is important to thoroughly clean the mold before storage. If possible, a bake-out (see Mold Life Extension, Paragraph c), followed by wiping the mold with a solvent, is best. If a bake-out is not possible, wiping the mold out with an aggressive solvent such as toluene will still help considerably. After cleaning the mold, apply a thin film of DOW CORNING 200® Fluid (low viscosities of 20, 50, or 100 centistokes are best). Placing a master of wax, plaster or wood in the mold will help retain the mold's shape.

–CAUTION–

Always provide adequate ventilation when using any solvent. In addition, all solvents should be completely evaporated before catalyzed RTV rubber is applied to the master pattern. When using any solvent, avoid heat, sparks and open flame. Follow the manufacturer's directions on container labels, including precautionary handling statements.

SAFE HANDLING INFORMATION

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DOW CORNING

SILICONE

MOLDMAKING

MATERIALS
FROM
DOW CORNING

A step-by-step guide
to product selection

DOW CORNING

S I L I C O N E

MOLDMAKING

MATERIALS FROM DOW CORNING

Create quality reproductions, time after time.

If you're looking for an easy-to-use moldmaking material that will deliver consistently superior results, look no further. With silicone moldmaking materials from Dow Corning, you can create tough-but-flexible molds to reproduce intricate details and deliver high-quality replicas, again and again. Remember, the closest thing to a reproduction from a silicone mold is the original itself.

We make a variety of products to meet a variety of needs: from reproduction of figurines, collectibles, jewelry, candles, and artifacts; to molding of prototypes, industrial tooling, and furniture; to creating silicone rubber pads for transfer printing and robotic skins for animated creatures; to architectural fabrication. Our products can be used with masters made of stone, glass, wood, metal, wax, ceramic, plaster, and clay. And they're compatible with a wide range of casting materials.

Each product consists of two components: a liquid silicone rubber base and a catalyst or curing agent. There are two basic cure types — condensation cure and addition cure — each containing several products in a range of viscosities with variable cure times. To identify the product(s) best suited to your application, start by using the product selection tree and typical moldmaking variables chart in Step 1.

STEP 1

NARROW THE FIELD TO MATCH YOUR NEEDS.

Silicone Moldmaking Materials from Dow Corning

- Are easy to use.
- Reproduce intricate details.
- Hold severe undercuts.
- Feature excellent natural release characteristics.
- Offer tailorable working times and cure rates.
- Are flexible to reduce demolding and stress problems.
- Provide good resistance to most chemicals.
- Resist tearing with repeated use.
- Work in a wide range of service temperatures.

Condensation Cure Products

***Dow Corning*® Brand Silicone Rubbers**

- For molding figurines, decorative reproduction, and making transfer pads.
- Provide outstanding resistance to inhibition.
- Use tin catalyst.
- Offer variable cure times at room temperature.

***Dow Corning*® HS II RTV High Strength Moldmaking Silicone Rubber.** Highest tear strength, low durometer (hardness). Well-suited for one-part molds.

***Dow Corning*® HS III RTV High Strength Moldmaking Silicone Rubber.** High tear strength, lower durometer. Well-suited for one-part molds.

***Dow Corning*® HS IV RTV High Strength Moldmaking Silicone Rubber.** High tear strength, lowest durometer, lowest mixed viscosity. Well-suited for one-part molds.

***Dow Corning*® 3110 RTV Silicone Rubber.** General purpose, low tear strength, medium durometer, low mixed viscosity, easy to work with, fills tiny crevices, vacuum de-airing isn't always required, white.

***Dow Corning*® 3112 RTV Silicone Rubber.** General purpose, low tear strength, high durometer, white.

***Dow Corning*® 3120 RTV Silicone Rubber.** Low tear strength, high durometer, excellent heat stability, red.

Addition Cure Products

***Silastic*® Brand Silicone Rubbers**

- For engineering design, prototyping, and architectural fabrication.
- Use platinum catalyst.
- Cure can be heat accelerated.
- Exhibit virtually no shrinkage when cured at room temperature.
- Offer better chemical resistance.

***Silastic*® E RTV Silicone Rubber.** Good tear resistance, low durometer (hardness), long working time, high elongation, white.

***Silastic*® J RTV Silicone Rubber.** Good tear resistance, high durometer, easy release, cut-growth resistance, green.

***Silastic*® L RTV Silicone Rubber.** Low durometer, soft and more flexible, high elongation, green.

***Silastic*® M RTV Silicone Rubber.** High tear strength, high durometer, good inhibition resistance, demoldable in 16 hours, regal blue.

***Silastic*® S RTV Silicone Rubber.** High tear resistance, very low durometer, low viscosity, high inhibition resistance.

***Silastic*® T-2 RTV Silicone Rubber.** Translucent/colorless, medium/low viscosity, low durometer, high inhibition resistance.

Typical Moldmaking Variables

	CONDENSATION CURE PRODUCTS						ADDITION CURE PRODUCTS					
	Dow Corning Silicone Rubber						*Silastic* Silicone Rubber					
	HS II	HS III	HS IV	3110	3112	3120	E	J	L	M	S	T-2
Pattern Characteristics												
Simple, no undercuts	●	●	●	●	●	●	●	●	●	●	●	●
Complex, some undercuts	●	●	●				●	●	●	●	●	●
Complex, deep undercuts	●	●	●				●	○	●	○	●	●
Vertical surfaces, large or immovable objects	●	●	●				●	●	●	○	●	●
Compatibility with Casting Materials												
Polyesters	●	●	●	○	○	○	●	○	○	○	●	○
Polyurethane, rigid	●	●	○	○	○	○	○	●	●	●	●	●
Polyurethane, foam	○	○		○	○	○	○	●	●	●	○	●
Epoxies				○	○	○	○	○	○	○	○	○
Low-melt metals				○	○	●	○	○	○	○	○	○

● *Recommended* ○ *Can be used*

STEP 2

TAKE A CLOSER LOOK AT YOUR CURE OPTIONS.

Once you've narrowed the field to a few materials, it's time to look at your cure options. *Dow Corning* HS II, HS III, and HS IV RTV High Strength Moldmaking Silicone Rubbers are available with the following catalysts:

- Clear, to allow custom coloring of the rubber.
- Colored pink, to aid inspection for uniform blending.
- Clay (HS II and HS III only), for curing against sulfur-containing clays. Colored green to aid inspection for uniform blending.

Dow Corning 3110, 3112 and 3120 RTV Silicone Rubbers can be used with either *Dow Corning*® 1 Catalyst or faster-acting *Dow Corning*® 4 Catalyst.

Each *Silastic* RTV Silicone Rubber has its own special curing agent. For best results, these products should be used in kit form as supplied, and only at the specified ratios.

The chart at right can help you determine the mix ratios, working times, and cure times most compatible with your equipment capabilities and application requirements.

Working and Cure Times at RT (72 ± 2°F, 23°C)

	Catalyst or Curing Agent	Base/Catalyst Mixing Ratio, By Weight	Approximate Working Time[1]	Approximate Demold Time[2]
CONDENSATION CURE	***Dow Corning* HS RTV High Strength Moldmaking Silicone Rubbers**			
	Dow Corning® HS II Catalyst	20:1 Clear	2 hrs	24 hrs
		10:1 Clear	45 min	16 hrs
		10:1 Colored	1-1/2 hrs	18 hrs
		10:1 Clay	45 min	16 hrs
	Dow Corning® HS III Catalyst	10:1 Clear	2 hrs	24 hrs
		10:1 Colored	2 hrs	24 hrs
		10:1 Clay	1 hr	16hrs
	Dow Corning® HS IV Catalyst	10:1 Clear	1 hr	24 hrs
		10:1 Colored	1 hr	24 hrs
	***Dow Corning* 3110 Silicone Rubber**			
	Dow Corning® 1 Catalyst	5:1	1 hr	5 hrs
		10:1	2 hrs	7 hrs
		20:1	3 hrs	12 hrs
	Dow Corning® 4 Catalyst	100:1	3 min	10 min
		200:1	5 min	20 min
		400:1	20 min	2 hrs
	***Dow Corning* 3112 Silicone Rubber**			
	Dow Corning 1 Catalyst	5:1	1/2 hr	6 hrs
		10:1	1 hr	8 hrs
		20:1	2 hrs	12 hrs
	Dow Corning 4 Catalyst	100:1	2 min	10 min
		200:1	5 min	20 min
		400:1	15 min	1-1/2 hrs
	***Dow Corning* 3120 Silicone Rubber**			
	Dow Corning 1 Catalyst	5:1	1/2 hr	6 hrs
		10:1	1 hr	8 hrs
		20:1	2 hrs	12 hrs
	Dow Corning 4 Catalyst	100:1	2 min	10 min
		200:1	5 min	1-1/2 hrs
		400:1	15 min	2-1/2 hrs
ADDITION CURE	***Silastic* Silicone Rubbers**			
	Silastic® E Curing Agent	10:1	1-1/2 hrs	24 hrs
	Silastic® J Curing Agent	10:1	2 hrs	24 hrs
	Silastic® L Curing Agent	10:1	1 hr	24 hrs
	Silastic® M Curing Agent	10:1	1 hr	16 hrs
	Silastic® S Curing Agent	10:1	45 min	7 hrs
	Silastic® T-2 Curing Agent	10:1	2-1/2 hrs	10 hrs

[1] *The time it takes for the catalyzed mixture to become nonflowable.*
[2] *The point at which the rubber can be demolded.*

STEP 3

FOCUS ON YOUR SPECIFIC PERFORMANCE OBJECTIVES.

When you've determined which products have the general performance and cure capabilities you need, review the following typical properties charts to see how these products match up with the specific properties you require.

Typical Properties†

	ADDITION CURE MATERIALS					
	Silastic Silicone Rubber					
	E	J	L	M	S	T-2
As Supplied						
Specific Gravity	1.12	1.28	1.27	1.29	1.12	1.12
As Catalyzed						
Appearance	White	Green	Green	Regal Blue	Green	Translucent
Viscosity, poise	500	900	1000	900	128	550
As-Cured Physical Properties[1]						
Durometer Hardness, Shore A, points	37	56	34	59	26	42
Tensile Strength, psi	800	900	550	650	1000	800
Elongation, percent	350	250	350	250	900	300
Tear Strength, die B, ppi	110	90	50	90	140	120
Useful Temperature Range, degrees	← -55 to 200°C (-67 to 392°F) →					
Linear Shrink, percent						
After 24 hrs @ 77°F (25°C)	Nil[2]	Nil[2]	Nil[2]	Nil[2]	Nil[2]	Nil[2]
After 7 days @ 77°F (25°C)	0.1	0.1	0.1	0.1	0.1	0.1

† *These values are not intended for use in preparing specifications.*
[1] *Based on sample thickness of 125 mils, cured 24 hours at room temperature.*
[2] *Shrinkage not measurable after curing 24 hours at room temperature.*

Typical Properties†

	CONDENSATION CURE MATERIALS											
	Dow Corning High Strength Moldmaking Silicone Rubber									*Dow Corning* Silicone Rubber		
	HS II				HS III			HS IV		3110	3112	3120
As Supplied												
Specific Gravity	1.21				1.16			1.16		1.14	1.30	1.45
Catalyst Used	10:1 Clear	20:1 Clear	10:1 Colored	10:1 Clay	10:1 Clear	10:1 Colored	10:1 Clay	10:1 Clear	10:1 Colored	10:1 1 Catalyst	10:1 1 Catalyst	10:1 1 Catalyst
As Catalyzed												
Appearance	White	White	Pink	Green	White	Pink	Green	White	Pink	White	White	Red
Viscosity, poise	200	200	200	200	160	150	170	160	170	130	280	280
As-Cured Physical Properties[1]												
Durometer Hardness, Shore A, points	20	20	16	22	10	10	14	5	5	45	60	60
Shore 00, points	—	—	—	—	56	55	62	53	52	—	—	—
Tensile Strength, psi	400	600	550	450	350	400	350	350	350	400	700	900
Elongation, percent	325	500	500	325	550	575	425	675	675	175	130	120
Tear Strength, die B, ppi	125	140	130	120	100	110	110	110	100	20	30	40
Upper Temperature Limit, °C	200	200	200	200	200	200	200	200	200	200	200	300
Linear Shrink, percent												
After 24 hrs @ 77°F (25°C)	.20	.20	.26	.21	.23	.20	.01	0.14	0.14	—	—	—
After 7 days @ 77°F (25°C)	.30	.30	.48	.40	.48	.48	.21	0.15	0.15	—	—	—

† *These values are not intended for use in preparing specifications.*
[1] *Based on sample thickness of 125 mils, cured 24 hours at room temperature.*

OTHER DOW CORNING PRODUCTS FOR THE MOLDMAKING INDUSTRY.

Dow Corning® **Thixo Additive.** This clear liquid can be used with *Dow Corning* HS II, HS III, and HS IV RTV High Strength Moldmaking Silicone Rubbers and *Silastic*® E, J, L, S and T-2 Silicone Rubbers to produce skin molds on vertical surfaces or from immovable objects.

Dow Corning® **Sprayable Catalyst** (Clear and Purple). This catalyst can be used with *Dow Corning* HS II and HS III Bases. Primary uses include robotic skins and tooling.

Dow Corning® **Q3-6559 Cure Accelerator.** Can be used to speed room-temperature cure of all *Silastic* RTV Silicone Rubbers and as a surface treatment to prevent inhibition. Contains a silicone polymer and platinum catalyst.

Dow Corning® **236 RTV Dispersion.** White; one-part coating. Used to prevent casting resins from sticking to wooden molding boxes/frames.

Dow Corning® **200 Fluid.** Used as a thinner to lower mixed viscosity. Also used as a release agent.

Dow Corning® **732 RTV Multi-purpose Sealant.** A one-part adhesive used to repair torn molds.

Dow Corning® **92-009 Dispersion Coating.** A one-part, room-temperature-cure coating used for painting silicone robotic skins; easily pigmented.

NEED MORE INFORMATION?

For general assistance or more information about product selection, call your Dow Corning sales representative or distributor.

For technical support or moldmaking advice, call our moldmaking experts, Bob Kelly at (517) 496-4462, or Customer Service at (517) 496-6000.

For technical data sheets, use Dow Corning's convenient Select-A-FAX system. With Select-A-FAX, you get free 24-hour access to the product information you need. Just follow these simple instructions:

1. Call 1-800-FAX-DC (1-800-443-2932) on your touchtone phone.
2. At the prompt, enter your FAX number and telephone extension.
3. When asked, speak (and spell) your name. Then, name your company and provide your telephone number.
4. When prompted, enter the Literature Code(s) for the product information you require. (Enter 22 at this step to receive the Moldmaking Industry Index, which provides Literature Codes for all moldmaking product sheets.)
5. Go to your FAX machine — the information you requested is on its way.

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Midland, Michigan 48686-0994

DOW CORNING

BB&Co.

CHOOSING A MOLDING TECHNIQUE

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There are three basic types of molds: block molds, glove molds, and brush-on molds. The best type to use for a particular object depends on its shape, intricacy, size and mobility.

TYPES OF MOLDS

Characteristics of Original		Suggested Molding Technique	Advantages
• A "flat back" • No deep undercuts		One-part block mold	• Fastest and easiest molding technique • Casting material can be poured • Casting material can be leveled with a spatula or by gentle vibration
• Detail on all sides • No deep undercuts		Two-part block mold	• Thick, durable mold • Easy to handle • Easy to demold • Ideal for use with casting material that should cool down slowly or for faster curing of some catalyzed resins
• A "flat back" • Deep undercuts and fine detail on the other side		One-part glove mold	• Easy to demold • Ideal for casting materials requiring quick cool-down
• Detail and undercuts on all sides		Two-part glove mold	• Very complex shapes can be reproduced • Easy to demold • Multipart molds are possible
• Large size • Extreme undercuts • Original cannot be moved		Brush-on skin mold	• Easy to demold, even with complicated originals • Economical for large originals

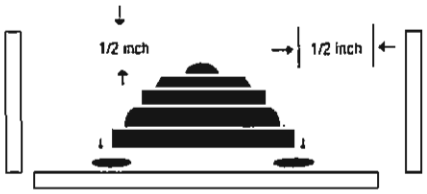
Making silicone molds

ONE-PART BLOCK MOLD

Step 1.

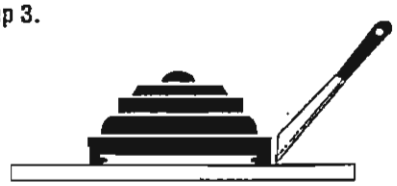
Prepare the original.

Step 2.



Prepare a molding box of wood, plastic or metal, making sure there is a minimum clearance of 1/2 inch between the edges of the original and the sides of the box, and a minimum clearance of 1/2 inch between the highest point of the original and the top of the box sides.

Step 3.



Mount the original to the base of the molding box. This can be accomplished by putting a strip of inhibitor-free modeling clay* around the edge of the back of the original. Press the original firmly onto the box base. For a more secure mounting, drill a hole in the center of the base and attach the original to the base with a wood screw.

Step. 4

Construct the molding box around the original. Carefully seal around the edges of the box and between the original and the box with sulfur-free pattern (filleting) wax or inhibitor-free modeling clay. This is necessary to prevent the liquid silicone rubber from seeping out. If you prefer castings with a smooth, high-gloss finish, ensure that the original is highly polished.

Step 5.

Prepare the molding material and pour it into the box, holding the container as close to the box as possible. Pour slowly to allow the material to fill all the crevices and level off. Continue pouring until the top of the silicone material is a minimum of 1/2 inch above the highest point of the original.

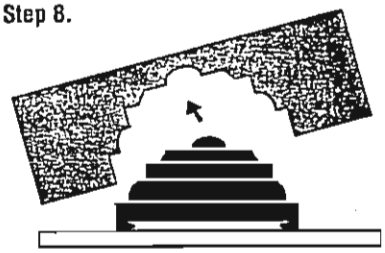
Step 6.

Cure for 24 hours at room temperature.

Step 7.

Remove the wax or clay sealing the sides of the box and disassemble the box.

Step 8.



Separate the mold from the original.

Silicone Moldmaking Material

*See "Modeling Clay" on "Suppliers of Moldmaking Equipment and Materials," Form No.10-525.

.WO-PART BLOCK MOLD

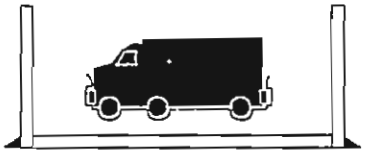
Step 1.

Prepare the original.

Step 2.

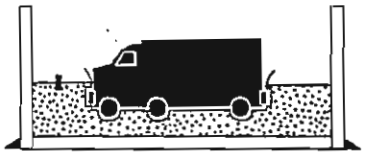
Prepare a molding box with sides, base and lid of wood, plastic or metal, making sure there is a minimum clearance of 1/2 inch around the original.

Step 3.



Seal the edges of the box with sulfur-free filleting wax or inhibitor-free modeling clay.

Step 4.

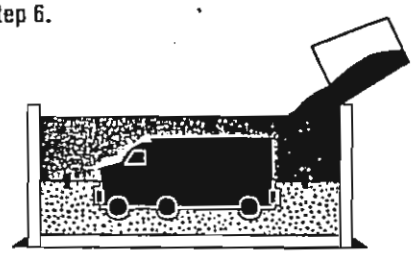


Wrap, in aluminum foil or plastic wrap, the half of the original that will be embedded in clay in the bottom of the box. Embed the original up to the pre-established parting line.

Step 5.

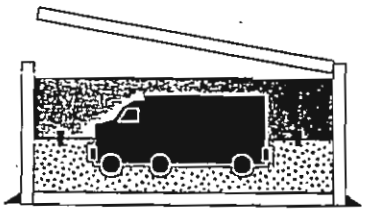
Insert alignment pegs into the clay.

Step 6.



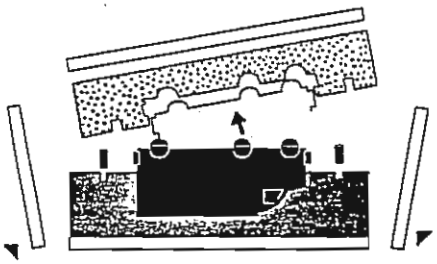
Prepare the molding material and pour it into the box, holding the container as low as possible. Pour slowly to allow the material to fill all the crevices and level off. Continue pouring until the top of the silicone material is a minimum of 1/2 inch above the highest point of the original.

Step 7.



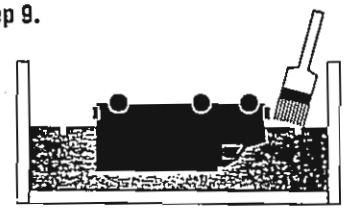
Cure for 24 hours at room temperature.

Step 8.



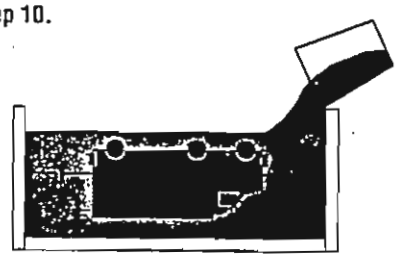
Invert the box and disassemble it. Remove the clay, foil or plastic wrap, and alignment pegs.

Step 9.



Reassemble the box and apply a release agent to the exposed area of silicone.

Step 10.

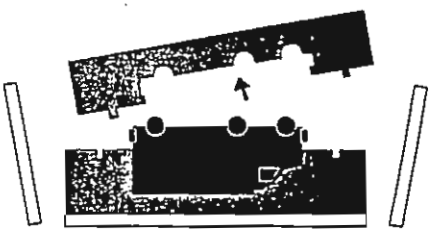


Holding the container as close to the box as possible, pour in the silicone material. Pour slowly to allow the material to fill all the crevices and level off. Continue pouring until the top of the silicone material is a minimum of 1/2 inch above the highest point of the original.

Step 11.

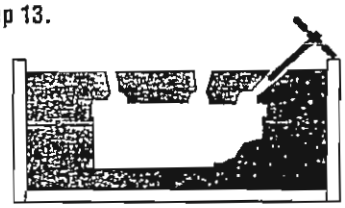
Cure for 24 hours at room temperature.

Step 12.



Disassemble the box and separate both parts of the mold from the original.

Step 13.



To prepare the mold for casting, drill two or more holes through it. The casting material will be poured into the mold cavity through one hole, and the air will escape through the other(s).

NOTE: If the original is relatively simple and not too large, it is possible to omit the use of the clay. Instead, pour the silicone material directly into the box to form the first half of the mold.

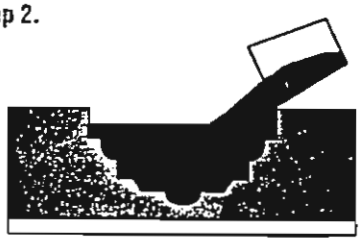
Casting into a silicone mold

ONE-PART BLOCK MOLD

Step 1.

Prepare the casting material according to the manufacturer's instructions.

Step 2.



With the mold on a flat, level surface, pour the casting material slowly into the mold, holding the container of casting material as close to the mold as possible. Brushing, vibrating or gently shaking will help to ensure that the casting material flows into all the crevices.

Step 3.

When the casting material has set, separate the mold from the casting using a firm, even pressure.

Step 4.

Smooth any rough edges by light filing or sanding.

NOTE: For easier demolding, some one-piece block molds require cutting. A predetermined parting line is marked on the master prior to casting the silicone mold. Once the master is removed from the mold, the seam line is matched up and the mold is held together, usually with rubber bands or tape.

■ Silicone Moldmaking Material

TWO-PART BLOCK MOLD

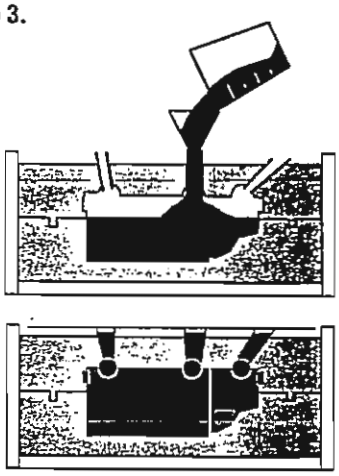
Step 1.

Reassemble the mold in the original molding box, ensuring that all parts are held firmly together.

Step 2.

Insert lengths of plastic tubing into the drilled holes. The plastic tubing in the air-escape hole(s) should protrude 1/2 inch from the mold. The plastic tubing in the filler hole must be long enough to reach above the top edge of the mold when it is in casting position.

Step 3.



Prepare the casting material according to the manufacturer's instructions.

With the mold in casting position, pour the casting material into the mold through a funnel inserted in the end of the filler tube. Hold the container of casting material as close to the funnel as possible. Keep pouring slowly until material rises in the air-escape tube(s). Vibrate or gently shake the mold so the material flows into all the crevices and any trapped air bubbles rise through the air-escape tube(s).

When casting with certain casting resins, it is necessary to cover the plastic tubes with a sheet of paper or plastic to prevent inhibition.

Step 4.

When the casting material has set, separate the mold from the casting using firm, even pressure.

Step 5.

Remove the plastic tubing and cut off the runners. Smooth any rough edges by light filing or sanding.

NOTE: If the casting is large or intricate, it may be advisable to pour the casting material into the mold until it is half full, vibrate or de-air it in a vacuum chamber, and then pour in the rest of the casting material.

Making silicone glove molds

ONE-PART GLOVE MOLD

Step 1.

Prepare the original.

Step 2.

Prepare a molding box of wood, plastic or metal, making sure there is a minimum clearance of 1/2 inch around the original.

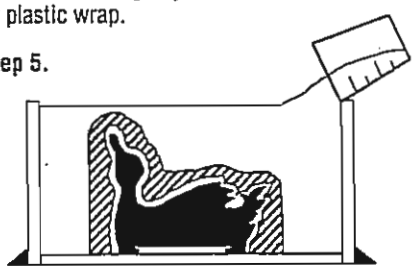
Step 3.

Place a strip of inhibitor-free modeling clay around the edge of the back of the original. Press the back of the original firmly onto the molding box base. Remove all excess clay. Mark the position of the original on the base.

Step 4.

Cover the original with aluminum foil or plastic wrap. Then apply a 1/8-inch layer of inhibitor-free modeling clay over the aluminum foil or plastic wrap.

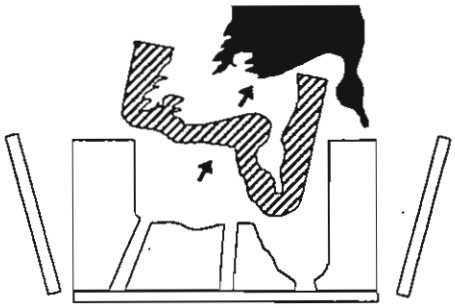
Step 5.



Assemble the molding box around the original. Pour a backing material, such as plaster, urethane resin, etc., into the box until it is full. Allow it to set until fully hardened. This is usually referred to as the "mother mold."

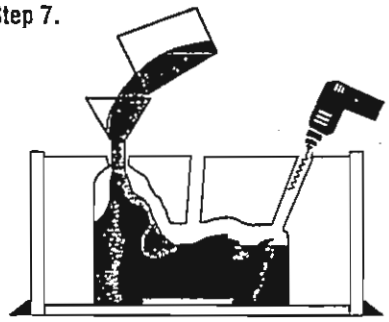
NOTE: Fiberglass-reinforced polyester can also be used to make lightweight counter molds or one- and two-part glove molds.

Step 6.



Disassemble the box. Lift off the mother mold and make one filler hole and several air-escape holes in it. Remove the clay and the aluminum foil or plastic wrap from the original.

Step 7.

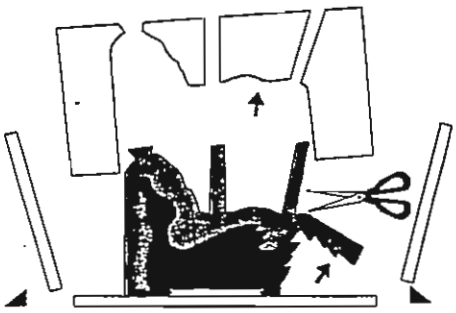


Put the mother mold and the reassembled box back in position over the original. Pour the silicone material slowly into the filler hole in the mother mold. Continue pouring until silicone material comes up the air-escape holes.

Step 8.

Cure for 24 hours at room temperature.

Step 9.



Disassemble the box, remove the mother mold and peel the silicone rubber from the original.

TWO-PART GLOVE MOLD

Step 1.

Prepare the original.

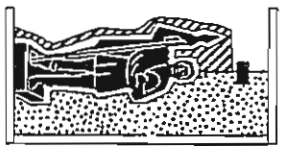
Step 2.

Prepare a molding box with sides, base and lid of wood, plastic or metal, making sure there is a minimum clearance of 1/2 inch around the original.

Step 3.

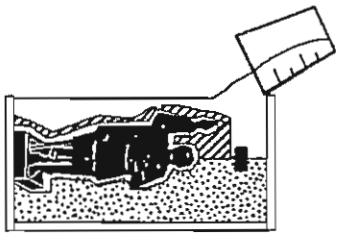
Wrap the original in aluminum foil or plastic wrap. Fill the box with presoftened clay. Embed the original in the clay up to the pre-established parting line.

Step 4.



Cover the visible half of the original with a 1/8-inch layer of inhibitor-free modeling clay. Insert alignment pegs into the clay.

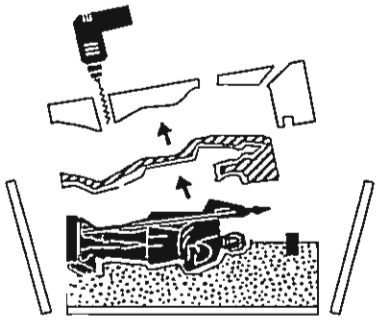
Step 5.



Pour the backing material over the original until it is completely covered. Allow it to set until fully hardened.

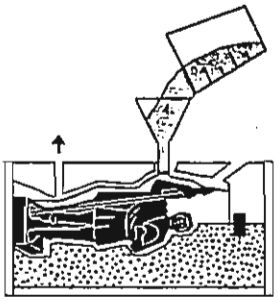
Continued on next page

Step 6.



Disassemble the box. Lift off the mother mold and make one filler hole and several air-escape holes in it. Discard the layer of clay. Remove the aluminum foil or plastic wrap from the exposed half of the original.

Step 7.

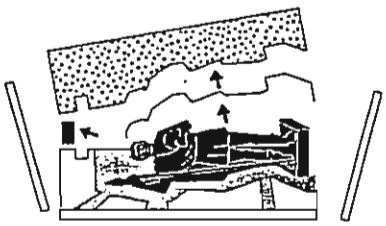


Put the mother mold and the reassembled box back in position over the original. Prepare the molding material and pour it slowly into the filler hole in the mother mold. Continue pouring until silicone material comes up the air-escape holes.

Step 8.

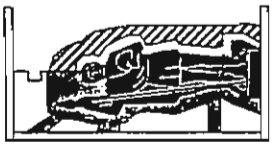
Cure for 24 hours at room temperature.

Step 9.



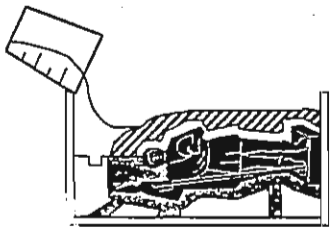
Invert the box and disassemble it. Remove and discard the clay filling half of the box and the alignment pegs.

Step 10.



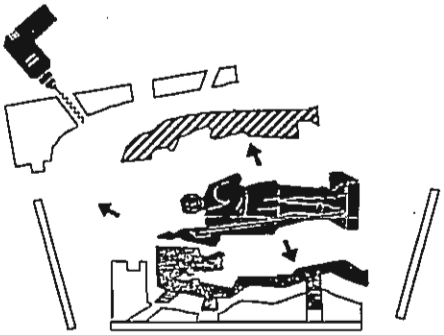
Reassemble the box and apply a release agent to the inside. Cover the visible half of the original with a 1/8-inch layer of inhibitor-free modeling clay.

Step 11.



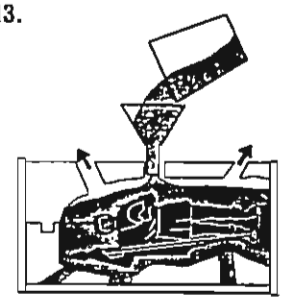
Pour backing material over the original until it is completely covered. Allow it to set until fully hardened.

Step 12.



Disassemble the box. Lift off the mother mold and make one filler hole and several air-escape holes in it. Discard the layer of clay and the remaining aluminum foil or plastic wrap.

Step 13.

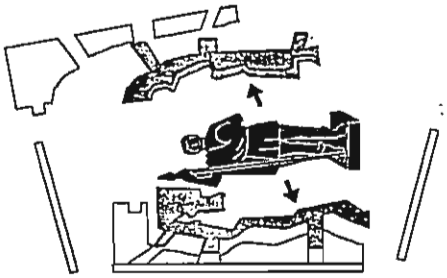


Put the mother mold and the reassembled box back in position over the original. Prepare the molding material and pour it slowly into the filler hole in the mother mold. Continue pouring until silicone material comes up the air-escape holes.

Step 14.

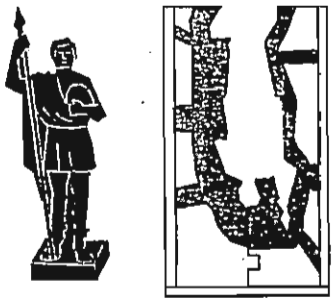
Cure for 24 hours at room temperature.

Step 15.



Disassemble.

Step 16.



To prepare the mold for casting, drill two or more holes through it. The casting material will be poured into the mold cavity through one hole and the air will escape through the other(s).

Silicone Moldmaking Material

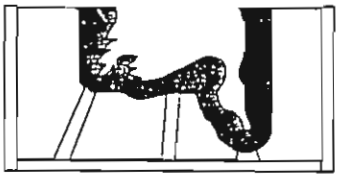
Casting into a silicone glove mold

ONE-PART GLOVE MOLD

Step 1.

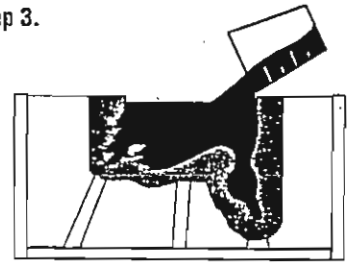
Reassemble the glove mold in the mother mold in the molding box.

Step 2.



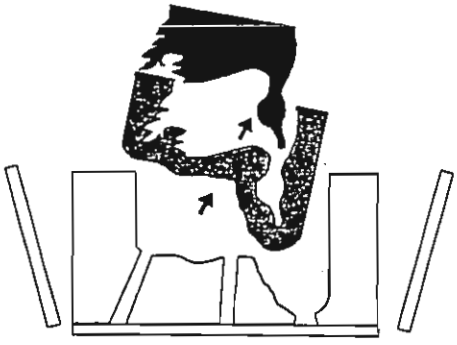
Prepare the casting material according to the manufacturer's instructions.

Step 3.



With the mold on a flat, level surface, pour the casting material slowly into the mold, holding the container of casting material as close to the mold as possible. Brushing, vibrating or gently shaking will help to ensure that the casting material flows into all the crevices.

Step 4.



When the casting material has set, remove it from the mold using firm, even pressure.

TWO-PART GLOVE MOLD

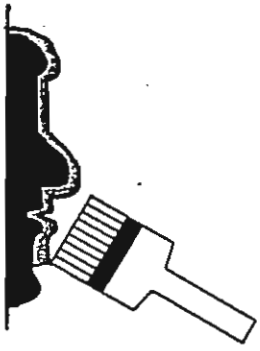
Replace the glove mold in the two halves of the counter mold and clamp them firmly together. Proceed as for a two-part block mold, described on page 4.

Making a brush-on skin mold

Step 1.

Prepare the original.

Step 2.



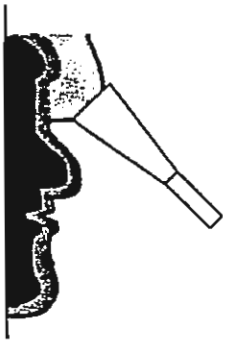
Paint the original with a thin precoat of base and catalyst mixture. This coating should be applied by brushing, and, to ensure a void-free coating, the mixture should be de-aired prior to use.

If air bubbles form during application of the RTV material, break them with a light air spray or by hand.

Cure at room temperature until the surface is tacky.

> NOTE: Increasing the ratio of the catalyst to base will accelerate curing so the coating will become tacky much faster. This also will result in a thicker skin layer on the original.

Step 3.



Prepare a mixture of thixotropic material following the instructions supplied with the product.

Step 4.

Using a brush or spatula, cover the precoat with a 1/4- to 3/8-inch layer of the thixotropic coating. If the original is large, it is advisable to prepare the thixotropic coating in several batches, applying it to one section at a time.

> NOTE: To smooth the surface of the thixotropic coating, dip a spatula in DOW CORNING 200® fluid, 50 cs, and groom the surface. Or wet a wash cloth and tap the surface of the skin mold to flatten the peaks. (The extra moisture will aid in the cure of the tin-cured rubbers.)

Step 5.

Cure for 24 hours at room temperature. Support the skin mold with a counter mold of glass-fiber-reinforced polyester, plaster or urethane foam.

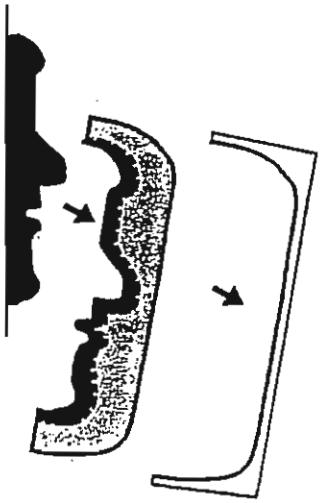
■ Thixotropic Material

Continued on next page

Casting a brush-on skin mold

BRUSH-ON SKIN MOLD *Continued*

Step 6.



Carefully remove the counter mold and place it securely on a horizontal surface.

Step 7.

Peel the rubber from the original.

Step 8.

Reassemble the silicone mold in the counter mold.

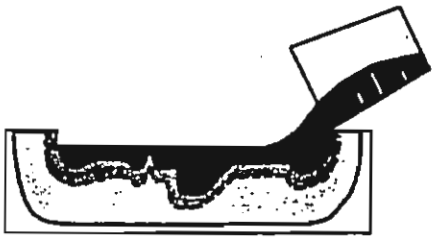
Silicone Moldmaking Material

Thixotropic Material

Step 1.

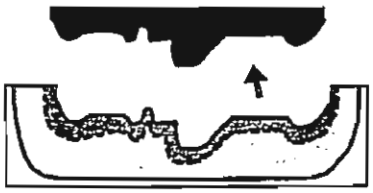
Position the mold in casting position in its counter mold. Prepare the casting material according to the manufacturer's instructions.

Step 2.



Pour the casting material slowly into the mold, holding the container of casting material as close to the mold as possible. Brushing, vibrating or gently shaking will help to ensure that the casting material flows into all the crevices.

Step 3.



When the casting material has set, separate the mold from the casting using a firm, even pressure.

Step 4.

Smooth any rough edges by light filing or sanding.

Dow Corning believes that the information in this publication is an accurate description of the typical characteristics and/or uses of the product or products, but it is your responsibility to thoroughly test the product in your specific application to determine its performance, efficacy and safety. Suggestions of uses should not be taken as inducements to infringe any particular patent.

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Midland, Michigan 48686-0994

DOW CORNING

GE Silicones

One-Component RTV Adhesive Sealants

PRODUCT DESCRIPTION

RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 one-component, ready-to-use adhesive sealants are extremely versatile. They cure to a tough, durable, resilient silicone rubber on exposure to atmospheric moisture at room temperature. Acetic acid vapors are released from the sealant surface as a by-product of cure.

RTV102, RTV103, RTV108 and RTV109 sealants are standard strength paste consistency products which can be applied to vertical and overhead surfaces where pourable/self-leveling sealants are not practical.

RTV112 and RTV118 sealants are self-leveling products which are preferable to paste-consistency sealants when flow into small crevices and hard-to-reach places is desired.

RTV106 sealant is paste-consistency sealant; RTV116 sealant is a self-leveling sealant. Both RTV106 and RTV116 sealants are standard strength high-temperature sealants.

Since all these sealants utilize a moisture cure system, they must not be used in thicknesses of greater than 6mm (1/4 in.).

Where section depths exceed 6mm (1/4 in.), GE Silicones two-component silicone rubber compounds are recommended.

KEY PERFORMANCE PROPERTIES

- One-component products
- Capability to cure at room temperature and ambient humidity
- Self adhesion properties
- Low temperature flexibility
- High temperature performance
- Excellent weatherability and ozone and chemical resistance
- Excellent electrical insulation properties

APPLICATIONS

Product	Features	Potential Applications	UL	Food Contact
RTV102 White RTV103 Black RTV108 Translucent RTV109 Aluminum	General purpose pastes	General purpose bonding, sealing, electrical insulation, formed-in-place gaskets. Can be applied to vertical or overhead surfaces.	File 36952	FDA 21 CFR 177.2600 USDA NSF Std. No. 51
RTV106 Red	High temperature paste	Sealing heating elements, gasketing, electrical insulation, and other critical bonding and sealing applications where parts must perform at high temperatures. Can be applied to vertical or overhead surfaces.	File 36952	FDA 21 CFR 177.2600 USDA NSF Std. No. 51
RTV116 Red	High temperature self leveling	Thin section potting, filling small surface voids, protective coating, electrical insulation where high temperature performance is required.	File 36952	FDA 21 CFR 177.2600 USDA NSF Std. No. 51
RTV112 White RTV118 Translucent	General purpose self leveling	Electrical insulation, thin section potting, protective coatings. Will flow into small crevices and hard to reach places.	File 36952	FDA 21 CFR 177.2600 USDA NSF Std. No. 51

These sealants were not designed for and should not be used for applications intended for permanent implantation into the human body.

These sealants are not for use in delicate electrical and electronic applications in which corrosion of copper, brass or other sensitive metals is undesirable.

TYPICAL PRODUCT DATA

Uncured Properties	RTV102, RTV103 RTV108, RTV109	RTV106	RTV116	RTV112, RTV118
Consistency	Paste	Paste	Self leveling	Self leveling
Color	RTV102 White RTV103 Black RTV108 Translucent RTV109 Aluminum	Red	Red	RTV112 White RTV118 Translucent
Viscosity, poises	–	–	250	200
Application Rate, (g/min)	400	400	–	–
Specific Gravity	1.05	1.07	1.09	1.05
Tack-Free Time, min.	20	20	30	20

Cured Properties[1]	RTV102, RTV103 RTV108, RTV109	RTV106	RTV116	RTV112, RTV118
Mechanical:				
Tensile Strength, kg/cm² (lb/in²)	28 (400)	26 (375)	25 (350)	23 (325)
Elongation, %	450	400	350	325
Hardness, Shore A	30	30	20	25
Tear Strength, kg/cm (lb/in)	8 (45)	7 (40)	–	–
Shear Strength, kg/cm² (lb/in²)[2]	14 (200)	14 (200)	7 (125)	7 (100)
Peel Strength, kg/cm (lb/in)[3]	7 (40)	7 (40)	3 (25)	3 (15)
Electrical:				
Dielectric Strength, kv/mm (v/mil)	20 (500)	20 (500)	16 (400)	16 (400)
Dielectric Constant @ 60 Hz	2.8	2.8	2.8	2.8
Dissipation Factor @ 60 Hz	.001	.001	.001	.001
Volume Resistivity, ohm-cm	$3x10^{15}$	$3x10^{14}$	$2x10^{14}$	$6x10^{14}$
Thermal:[4]				
Brittle Point, °C (°F)	-60 (-75)	-60 (-75)	-60 (-75)	-60 (-75)
Maximum continuous operating temperature, °C (°F)	204 (400)	260 (500)	260 (500)	204 (400)
Maximum intermittent operating temperature, °C (°F)	260 (500)	315 (600)	315 (600)	260 (500)
Additional Information:[4]				
Linear Shrinkage, %	1.0	1.0	1.0	1.0
Thermal Conductivity, cal/sec/cm², °C/cm (Btu/hr/ft², °F/ft)	.0005 (.12)	.0005 (.12)	.0005 (.12)	.0005 (.12)
Coefficient of Expansion cm/cm, °C (in/in, °F)	$27x10^{-5}$ ($15x10^{-5}$)	$27x10^{-5}$ ($15x10^{-5}$)	$27x10^{-5}$ ($15x10^{-5}$)	$27x10^{-5}$ ($15x10^{-5}$)

[1] Cure time 3 days/25C (77F)/50% relative humidity.
[2] At 100% cohesive failure.
[3] At 100% cohesive failure using 1 in. x 8 in. stainless steel screen at 180° pull angle.
[4] Information is provided for customer convenience only. These properties are not tested on a routine basis.

SPECIFICATIONS

Typical property data values should not be used as specifications. Assistance and specifications are available by contacting GE Silicones.

INSTRUCTIONS FOR USE

Surface Preparation

RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 sealants will bond to many clean surfaces without the aid of primers. These surfaces typically include many metals, glass, ceramic, silicone rubber and some rigid plastics. These adhesive sealant products will also produce fair bonds to organic rubber and to some flexible plastics not containing fugitive plasticizers (which migrate to the surface, impairing adhesion). An evaluation should be made to determine bond strength for each specific application. For difficult-to-bond substrates, use of a primer is suggested. Primers SS4004, SS4044 and SS4179 are recommended for use with these sealants. (Complete information and usage instructions for these primer products are contained in a separate product data sheet, CDS1532).

Where adhesion is required, surfaces should be thoroughly cleaned with a suitable solvent such as naphtha or methyl ethyl ketone (MEK) to remove dirt, oil and grease. The surface should be wiped dry before applying the adhesive sealant.

When solvents are used, proper safety precautions must be observed.

Application and Cure Time Cycle

Paste-consistency products may be applied directly to clean or primed substrates. Where broad surfaces are to be mated, the sealant should be applied in a thin, less than 6mm (1/4 in.) diameter, bead or ribbon around the edge of the surface to be bonded.

Flowable products may be applied to clean or primed substrates by pouring directly from the original container or dipping. These products will self-level on a surface, filling small crevices and surface voids. Depth of potted sections should not exceed 6mm (1/4 in.).

The cure process begins with the formation of a skin on the exposed surface of the sealant and progresses inward through the material. At 25C (77F) and 50% relative humidity, RTV102, RTV103, RTV106, RTV108, RTV109, RTV112 and RTV116 sealants will form a surface skin which is tack-free to the touch in 15 to 30 minutes. Once the tack-free skin has begun to form, further tooling of the adhesive sealant is not advisable.

Higher temperatures and humidity will accelerate the cure process; low temperatures and low humidity will slow the cure rate.

As the adhesive sealant cures, acetic acid vapors are released from the sealant surface. The odor of acetic acid will completely disappear when curing is completed.

A 3mm (1/8 in.) section of adhesive sealant will cure through in approximately 24 hours at 25C (77F) and 50% R.H. Since cure time increases with thickness, use of these adhesive sealants should be limited to section thicknesses of 6mm (1/4 in.) or less.

Bond Strength Development

In addition to the effects of temperature and relative humidity, development of maximum bond strength will depend on joint configuration, degree of confinement, sealant thickness and substrate porosity. Normally, sufficient bond strength will develop in 12 to 24 hours to permit handling of parts. Minimum stress should be applied to the bonded joint until full adhesive strength is developed. Eventually the adhesive strength of the bond will exceed the cohesive strength of the silicone rubber sealant itself. Always allow maximum cure time available for best results.

PACKAGING AND DISPENSING

RTV adhesive sealants from GE Silicones are supplied ready-to-use in collapsible aluminum squeeze tubes, caulking cartridges and in bulk containers.

Collapsible aluminum tubes may be squeezed by hand or with the aid of mechanical wringers which allow more complete removal of material from the tube. Air-operated dispensing guns may also be used with aluminum tubes and offer the advantages of improved control and faster application for production line use. The sealant may be dispensed from caulking cartridges by using simple mechanical caulking guns or air-operated guns. Air-operated guns will allow greater control and application speed. Both tubes and cartridges are easy to use, can be put into production quickly and require minimal capital investment.

Note: Do not exceed 45 psig when used in air-powered caulking guns.

Bulk containers require a larger initial investment in dispensing equipment, but offer the most economical packaging for volume production. Bulk dispensing systems are air-operated extrusion pumps coupled to hand or automated dispensing units. Pumps which are specifically designed for pumping one-component RTV silicone rubber have TEFLON® seals, packings and lined hoses to prevent moisture permeation and pump cure problems. Specific details on dispensing systems and manufacturers are available in a separate GE Silicones RTV Silicone Rubber Equipment Guide (CDS1541).

CLEAN UP AND REMOVAL

Before curing, solvent systems such as naphtha or methyl ethyl ketone (MEK) are most effective. Refer to solvent use warnings in the section on surface preparation.

After cure, selected chemical strippers which will remove the silicone rubber are available from other manufacturers. Specific product information may be obtained on request.

FDA STATUS

RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 sealants can be used in food contact applications where FDA regulations apply. Reference CDS4319 "Food Contact Applications, Silicone Rubber Compounds", for specific regulations, limitations and conditions of use.

USDA STATUS

RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 sealants may be used on equipment which may contact edible products in official establishments operating under the Federal meat and poultry products inspection program. See USDA letter of Authorization.

NSF STATUS

The National Sanitation Foundation lists RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 sealants under NSF Standard No. 51 (Plastic Materials and Components for Use in Food Equipment), as satisfactory for use on food contact surfaces. Refer to GE bulletin CDS4319 before use.

UL STATUS

RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 silicone rubber adhesive sealants are cognized by Underwriters Laboratories, Inc., under their Component Recognition Program (UL File No. E-36952). Refer to CDS4320 for additional information.

MILITARY SPECIFICATION

MIL-A-46106B

Group I	Type I	General Purpose Paste RTV102, RTV103, RTV108, RTV109
	Type II	General Purpose Flowable RTV112, RTV118
Group III	Type I	High Temperature Paste RTV106
	Type II	High Temperature Flowable RTV116

Testing for referenced MIL Spec is performed in accordance with current GE Silicones quality test methods, laboratory conditions, and procedures, frequency and sampling, which are not necessarily identical with the methods, conditions, procedures, frequency and sampling stated or referenced in the listed specification. Any certification will be limited to listed properties and will not imply or state conformity to any other aspect of the referenced specification, including but not limited to marking, packaging, bar coding, testing, or sampling. Contact GE Silicones for a comparison review.

HANDLING AND SAFETY

These products are manufactured and sold for industrial use only.

Material Safety Data Sheets are available upon request from GE Silicones. Similar information for solvents and other chemicals used with our products should be obtained from your suppliers.

STORAGE WARRANTY PERIOD

When stored in the original unopened containers in a dry location at temperatures less than 27C (80F), RTV102, RTV103, RTV106, RTV108, RTV109, RTV112, RTV116 and RTV118 sealants offer a storage life of up to one year from date of shipment from the manufacturer.

AVAILABILITY

GE Silicones rubber sealants may be ordered from GE Silicones, Waterford, NY 12188, the GE Silicones Sales office nearest you or an authorized GE silicone product distributor.

GOVERNMENT REQUIREMENT

Prior to considering use of a GE Silicones product in fulfilling any Government requirement, contact GE Silicones Government Programs Office.

MITED WARRANTY

GE Silicones warrants that its product will conform to GE Silicones' internal specifications at the time of application or use, provided that the product is stored in accordance with GE Silicones' recommendations and used or applied before the earliest of (1) the "Use Before Date" indicated on the product package, (2) one year from date of shipment, or (3) expiration of such other period or recommended storage time stated in the GE Silicones' literature for the product. If notified in writing of a claim within six months of the product's use or application, GE Silicones will, at its option, replace or refund the purchase price of any GE Silicones product which does not satisfy the foregoing warranty.

THE FOREGOING SHALL CONSTITUTE THE SOLE AND EXCLUSIVE REMEDY FOR DEFECTS OR FAILURE OF THE PRODUCT, AND THE SOLE AND EXCLUSIVE LIABILITY OF GE. THE WARRANTIES STATED ABOVE ARE IN LIEU OF ALL OTHER WARRANTIES, WRITTEN OR ORAL, STATUTORY, EXPRESS OR IMPLIED, INCLUDING ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR PURPOSE.

LIMITATION OF LIABILITY: GE shall, in no event, whether the claim is based on warranty, contract, tort, strict liability, negligence or otherwise, be liable for incidental or consequential damages, or for any other damages in excess of the amount of the purchase price.

NOTE: For many products, GE Silicones may be able to offer a more extensive, application specific warranty. For further information, contact your GE Silicones field representative.

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CDS4312 (5/93)

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DLL: 7/98

Higgins

ABSTRACT

Hxtal NYL-1 an epoxy and Loctite 350 an acrylic adhesive have been evaluated for use in the conservation of glass, particularly the Portland Vase at The British Museum. The results of accelerated ageing of the adhesives using light and heat ageing regimes are reported. Hxtal NYL-1 was found to have good colour stability to light ageing but poor stability to heat ageing. It is reversible using solvents. The colour stability of pigmented samples of Hxtal resin was also investigated. Preparation of pigmented resin was found to be difficult, and the colours investigated exhibited some fading during light ageing. Loctite 350 was found to yellow slightly during both light and heat ageing and to be reversible using solvents followed by mechanical removal.

EVALUATION OF HXTAL NYL-1 AND LOCTITE 350 ADHESIVES FOR GLASS CONSERVATION

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INTRODUCTION

During 1981 and 1982 several epoxy and polyester resins were evaluated for use in the conservation of glass at The British Museum. The results of the accelerated ageing tests carried out at that time showed that exposure to heat at 70°C for 28 days caused greater yellowing of samples than exposure to an intense daylight spectrum lamp for 2000h. Since the results of the tests were reported (1) the samples have been exposed on a wall in the author's laboratory and subject to the normal daily cycle of natural daylight, artificial light and night time. In the intervening seven years the heat aged samples which were yellowed have remained unchanged indicating that the resins yellow to a finite extent, the light aged samples have darkened to an extent similar to the heat aged samples, and the control samples have yellowed to an extent which is intermediate between the initial colours of the light and heat aged samples. These results have led the author to conclude that the results of heat ageing must be considered together with the results of light ageing when evaluating the colour stability of resins using accelerated ageing tests. Although natural ageing may be a superior method of assessment (2) time considerations favour accelerated ageing tests.

Hxtal NYL-1 epoxy and Loctite 350 acrylic adhesives have been evaluated for general use in the conservation of glass in The British Museum and specifically for use in the conservation of the Portland Vase. Accelerated heat and light ageing regimes have been used to assess the stability of Hxtal NYL-1 a two component epoxy adhesive and Loctite 350 a light curing acrylic adhesive. Hxtal NYL-1 was introduced into conservation during 1982-83 by Mr H Hillary (4). It was reported to be a low viscosity, colourless, colour stable adhesive suitable for use as an adhesive for glass. The resin was described as an hydrogenated epoxy resin and the hardener as a polyoxypropylene triamine hardener with imidazole accelerator (5). Curing time was reported to be 20h to 7 days at ambient temperature.

Loctite 350, a light curing acrylic adhesive was developed for use with glass and introduced into conservation about two years ago. The one component, medium viscosity, modified methacrylic ester adhesive (6) is cured by ultraviolet light. A join has to be perfectly aligned before the light source is directed along it as the adhesive cures within seconds.

The effects of light and heat ageing on ease of reversibility and colour stability were determined. Fourier transform infrared spectroscopy was used to investigate two batches of Hxtal NYL-1 supplied by Mr Hillary and the effect of ageing on the cured adhesive. The adhesives were also evaluated for use in the conservation of the Portland Vase (7) and for this purpose the effect of ageing on pigmented samples of Hxtal NYL-1 was determined. The tensile strength of joins prepared with both adhesives was investigated.

EXPERIMENTAL

Sample Preparation

Samples were prepared on microscope slides which had been degreased with acetone. The adhesives were spread onto the slides to form thin films and allowed to cure.

Hxtal NYL-1

Two batches of Hxtal NYL-1 were received. Batch I was mixed 4:1, resin:hardener. Batch, II was said to have been improved by charcoal filtration of both the resin and hardener to improve the colour, and reaction of the resin with sodium borohydride. The latter presumably being to reduce any aldehydes, and ketone groups present to alcohol groups. This batch was mixed in the stoichiometric ratio of 3:1, resin:hardener (5).

Batch I of the Hxtal adhesive was often used pre-accelerated by the conservators. The resin was pre-accelerated by heating it above a beaker of boiling water for 15 minutes stirring occasionally. The effect of this heating was to speed up the rate of curing to approximately 24h. Therefore two sets of samples were prepared, one by mixing the two components as supplied, the other by mixing pre-accelerated resin with hardener. Batch II of the Hxtal adhesive was used as supplied only following discussions with Mr Hillary (5) who suggested that curing at 43°C after mixing the resin would result in a curing time of 24 hours or less.

Lisa Pilosi

Pigmented Hxtal NYL-1

Two methods of preparing transparent coloured fills in coloured glass were considered. These were making the fill from clear resin and painting the external surface of the fill with a pigmented lacquer, or adding pigment to the resin so that the fill would be coloured throughout. The latter approach was thought to be more suitable for use with a highly coloured glass.

A deep cobalt blue was needed and pigments currently in use in the Ceramics and Glass Section were selected for mixing into the Hxtal NYL-1 resin to prepare a suitably coloured resin. Mixing the colours into the resin was difficult, and it became apparent that the pigments would not disperse using any of the stirring facilities available to the section. The reason for this was diagnosed as the viscosity of the resin being too low to cut and dispere the pigment.

Mr Hillary produced three pigmented samples of resin using Phthalocyanine blue, Keyplast blue BGP and Key oxaxine violet prepared by mixing in a high speed blender or a ballmill for up to 24h, using clear Hxtal NYL-1 Batch II which had been heated to 49°C. All the samples were optically dense and the cobalt blue colour required was finally obtained by mixing Hxtal containing Keyplast blue BGP and Keyoxaxine violet with clear hxtal prior to mixing the resin with the hardener. Samples of the different colours were prepared by painting mixed resin and hardener onto microscope slides degreased with acetone. Pooling on the slides occurred which was prevented by degreasing with soap and water.

Loctite 350

Loctite 350 adhesive was spread on microscopic slides to form a thin film and exposed to a Flexiarc type UVLS101 lamp for 90 seconds. The surface of the adhesive did not fully cure. Silicone release paper was pressed against the partially cured surface before exposing the samples to the light source for a further 15 seconds. This resulted in full curing of the samples.

Joins

Test joins were prepared using Hxtal NYL-1 and Loctite 350 in microscope slides which had been cut in half with a glass cutter. The edges of the microscope slides were degreased using acetone prior to application of the adhesive. Hxtal NYL-1 Batch I was used pre-accelerated and as supplied.

Accelerated ageing regimes

Heat ageing was carried out to simulate ageing in the dark, the samples being placed in an oven at 70°C for 28 days. Light ageing was carried out in a Microscal Light Fastness tester with a daylight spectrum lamp and was continued until the samples showed signs of yellowing when examined visually.

Evaluation tests

Reversibility

The reversibility of the samples was assessed qualitatively before and after ageing by immersing fragments of coated microscope slides in acetone, toluene, dichloromethane and tetrahydrofuran in sealed sample tubes for 24h. Since neither Hxtal or Loctite adhesive dissolved in the solvents the reversibility was assessed by the extent to which the adhesive was separated from the glass.

Colour

The colour of the samples before and after ageing was determined by measuring their UV-visible reflectance spectrum samples in a Perkin Elmer 551S UV-visible spectrophotomer fitted with an integrating sphere. The CIE L* a* b* coordinates, and hence colour change (ΔE), were calculated from the spectra. ΔE was calculated using equation 1

$$\Delta E = [(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2] \qquad (1)$$

Where L_1^*, a_1^* and b_1^* are coordinates for the control sample

and L^*_2 a_2^* and b_2^* are coordinates for the aged sample.

Fourier Transform Infrared spectra

The Fourier transform infra red (FT-IR) spectrum of the Hxtal NYL-1 adhesives were obtained using a Perkin Elmer Model 1700 Fourier Transform Infra Red Spectrometer. The FT-IR spectrum of the uncured Hxtal resin and hardener and cured control, light aged and heat aged samples were obtained between 4000 and 400 cm^{-1}. The spectra were used to observe differences in the chemistry of the two batches of Hxtal NYL-1 adhesive and differences resulting from ageing of the adhesives.

Strength

The tensile strength of the joins was measured using a JJ Lloyd model 15003 bench top tensile testing machine. The tensile strength of the join was calculated using equation 2.

$$\text{Tensile strength} = \frac{\text{Force } Nm^{2}}{\text{area}} \qquad (2)$$

The variability coefficient of the measurements was calculated.

RESULTS

Clear Hxtal NYL-1 adhesive

Reversibility

The results of the reversibility tests on batch 1 of the adhesive are shown in Table I. The tests were not repeated for batch II of the adhesive.

Sample	Solvent			
	Acetone	Toluene	Dichloromethane	Tetrahydrofuran
Control	Disruption	Disruption	Separation	Separation
Light aged	No effect	Slight disruption	Separation	Separation
Heat aged	No effect	No effect	Separation	Separation

TABLE I

The adhesion of Hxtal NYL-1 to glass was found to be reversible in dichloromethane and tetrahydrofuran both before and after ageing.

Colour

The colour stability of batch I and II of Hxtal NYL-1 to ageing was determined. The UV visible spectra for all samples of Hxtal NYL-1 batch I are shown in Figure 1. The curves and the visual assessment indicate that only very slight yellowing of the adhesive occurred when exposed in the light fastness tester for 2000h. Severe yellowing occurred to the heat aged samples which were then exposed in the light fastness tester to determine whether yellowing was reversible by bleaching. Typical curves obtained for reversion of the effects of heat ageing on Hxtal NYL-1 batch I are also shown in Figure 1.

The CIE L* a* b* coordinates calculated from the curves and the colour change ΔE are shown in Table II.

Sample	CIE			ΔE
	L*	a*	b*	
HXTAL NYL-1 Batch I				
Control	90.287	-0.483	1.096	
light aged	90.530	-0.4880	1.039	0.249
heat aged	88.732	-4.742	13.041	12.775
& exposed to light 361h	89.613	-2.744	6.989	6.348
& exposed to light 4561h	90.471	-1.054	3.230	2.209
HXTAL NYL-I Batch 1				
PRE ACCELERATED				
Control	90.761	-0.510	1.061	
light aged	91.211	-0.722	1.471	0.644
heat aged	88.440	-5.720	17.297	17.208
& exposed to light 361h	87.713	-1.923	4.374	4.719
HXTAL NYL-1 Batch II				
Control	93.435	-0.288	0.631	
light aged	94.097	0.165	0.798	0.869
Control	93.331	-0.1556	0.471	
heat aged	91.990	-3.296	7.627	7.929

TABLE II

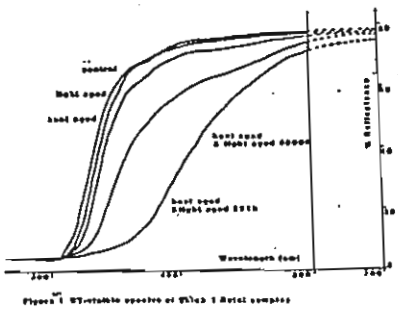

Figure 1 UV-visible spectra of Hxtal 1 Batch samples

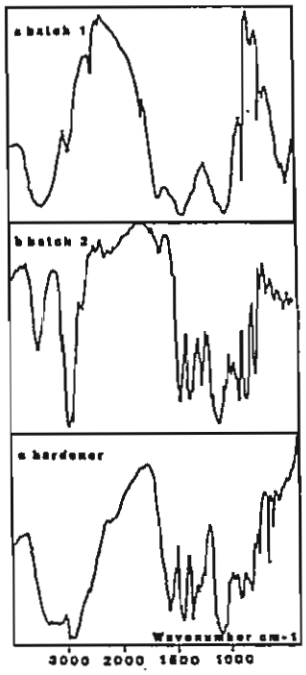

Figure 2 FT-IR spectra of Hxtal NYL-1 resins & hardener

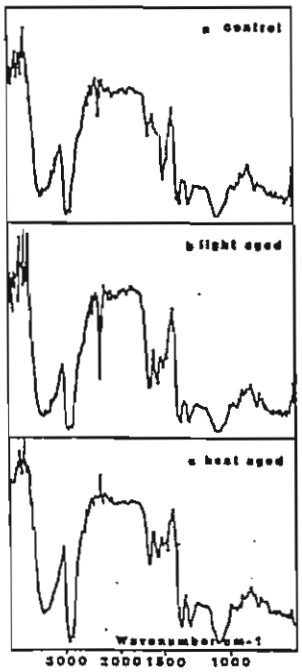

Figure 3 FT-IR spectra of cured control and aged Hxtal NYL-1 samples

The slight yellowing of Hxtal NYL-1 after 2000h of light ageing compares favourably with other expoxy systems (1) and is similar to results we have obtained for the yellowing of Paraloid B72 in the light fastness tester. Both batches of Hxtal yellowed during heat ageing, but this was less pronounced for batch II. Pre-accelerating batch I caused the Hxtal to yellow to a greater extent during both light and heat ageing. Exposing the batch I heat aged samples in the light fastness tester resulted in some reversal of the yellowing caused by heat ageing. The spectra of these samples were measured several times between 361 and 4561h exposure. Maximum reversal was obtained at 4000h exposure and further exposure to 4561h did not increase the extent of reversal. These results suggest that exposure of the adhesive to normal daily cycles of light and dark will result in some yellowing. Comparison with the results of previous ageing tests on epoxy resins discussed in the introduction suggest that the Hxtal NYL-1 adhesive is likely to yellow to a colour between that indicated by light ageing and that indicated by heat ageing.

Fourier Transform Infra-Red Spectra

Comparison of the spectra obtained for the batch I and batch II resins suggested that there were considerable differences between the two, see Figure 2a and b. It is not clear whether this was as a result of filtration and reaction of the batch II resin with sodium borohydride. The spectra of the hardener for both batches was identical, Figure 2c.

The spectra of cured samples of batch I and pre-accelerated batch I were identical, Figure 3a, as were those of the heat and light aged samples, Figures 3b and 3c. A change in the structure observed following heat and light ageing occurred in the region 1550-1720 cm^{-1}. Two peaks, 1600 and 1720 cm^{-1} were present in both control samples. The four heat aged and light aged samples exhibited peaks at 1720, 1640, 1600 and 1550 cm^{-1}. No substantial change was observed in any other part of the spectrum. The similarity in the spectra of the aged samples suggested that the results of the light and heat activated reactions were similar, although considerably more yellowing was apparent as a result of heat ageing. This was presumably caused by formation and conjugation of double bonds in the structure.

Pigmented Hxtal NYL-1 adhesive

Colour

The colour stability of the samples on light and heat ageing was determined. Light ageing was carried out for 1000h and heat ageing for 28 days at 70°C. The results of L* a* b* and ΔE calculations are given in Table III.

Sample			CIE L*	a*	b*	ΔE
Phthalocyanine	-	control	65.108	-34.807	-35.407	
blue	-	light aged	67.425	-32,710	-33.850	3.451
	-	heat aged	59.429	-43.934	7.769	44.978
Keyplast blue	-	control	46.029	8.464	-70.725	
	-	light aged	67.830	-15.213	-36.352	47.089
	-	heat aged	45.734	-9.595	-39.461	36.106
Keyoxaxine	-	control	17.017	25.256	-32.964	
violet	-	light aged	19.246	61.589	-66.458	49.452
	-	heat aged	24.860	40.025	-46.693	21.636
Keyblue violet:	-	control	27.081	44.883	-64.106	
clear hxtal	-	light aged	16.922	40.085	-54.279	14.926
1:1:2	-	heat aged	42.056	23.388	-57.977	26.904

TABLE III

The results show that the pigmented resin samples fade on exposure to light. The Keyplast blue and Keyoxaxine violet appear to be more stable to heat ageing than to light ageing.

Loctite 350 Adhesive

Reversibility

The reversibility of the adhesive was assessed qualitatively as described above and the results are given in Table VI.

Sample	Solvent: Acetone	Toluene	Dichloromethane	Tetrahydrufuran
Control	Softened	Softened and flaked	Swelled	Swelled with disruption
Light aged	Softened	Flaking	Disruption	Disruption
Heat aged	Softened	Flaking	Disruption	Disruption

TABLE IV

Colour

The colour stability of Loctite 350 adhesive to heat and light ageing was determined. A visual assessment of the aged samples indicated that some yellowing had occurred during both heat and light ageing. The UV-visible spectra of the samples were used to calculate CIE L* a* b* coordinates and hence colour change from the control sample ΔE. The results are given in Table V.

Sample	ΔE
Light aged	5.572
Heat aged	6.601

TABLE V

These results indicate that light and heat ageing cause yellowing to a similar extent.

Joins

Prepared joins were exposed in the light fastness tester for 2000h and heat aged for 28 days at 70°C.

Colour

The colour of the joins was assessed visually by comparison with control samples. None of the joins showed signs of yellowing.

Tensile Strength

The results obtained for the unaged joins are given in Table VI.

Sample	Tensile strength Nm^{-2} Mean	Range	Variability Coefficient
Hxtal NYL-1	7.0	3.5 - 9.8	13.2
Hxtal NYL-1 (pre-accelerated)	20.2	17.6 - 24.0	23.0
Loctite 350	28	26 - 33	15.7

TABLE VI

The number of samples measured was small, being six in each group. The variability of the results indicated that many more samples would need to be tested to give significant tensile strength values. However the general trend of the results is that Loctite 350 adhesive gives a stronger bond in clear glass than Hxtal NYL-1.

The measurements made on aged joins were highly variable and did not indicate any trend towards reduction or increase in adhesion.

Discussion

The results of the tests suggest that Hxtal NYL-1 is a light stable adhesive, but in common with other epoxy adhesives is subject to yellowing when heat aged. The results of bond strength tests were too variable to indicate either an increase or decrease in bond strength on ageing. The ageing of pigmented samples of Hxtal NYL-1 suggested that some colour change may occur under normal display conditions in a museum. In reversibility tests Hxtal NYL-1 was more readily separated from glass than was Loctite 350, although removal could be achieved by a combination of softening in solvent followed by mechanical removal.

Loctite 350 adhesive yellowed in both light ageing and heat ageing suggesting that yellowing will occur during the lifetime of the adhesive on an artefact (50-100 years). However the handling properties of Loctite 350 and the bond strength achieved in clear glass were superior to those of Hxtal NYL-1. The results of tests on both adhesives indicate that they are useful materials to be added to the repetoire of glass conservators.

Taking into account all of the observations the procedure chosen for repair of the Portland Vase was to first tack the joins using spots of Loctite 350 cured with a UV light source. This allowed the vase to be constructed in sections and the alignment of joins to be checked before they were finally adhered using Hxtal NYL-1 (batch I). Joins which were incorrectly aligned were reversed by using dichloromethane to soften the Loctite adhesive. This process was easier than predicted from experimental work, perhaps suggesting that the blue glass of the vase affected the cure of the adhesive. Gaps in the fabric of the vase were filled using pigmented Hxtal NYL-1 (batch II). An appropriate colour was achieved using a mixture of Keyplast blue, Key Oxaxine violet and clear Hxtal. The vase has now been returned to exhibition in The British Museum where the effects of the conservation can be seen (7).

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Material Suppliers

Pigments, Keystone Aniline Corporation of Chicago, USA.

Loctite 350, Loctite UK, Loctite Holdings Ltd, Watchmead, Welwyn Garden City Herts AL7 1JB.

Hxtal NYL-1, Mr H Hillary, 1909 Richcreek Rd, Austin, Texas 78757, USA.

Health and Safety

Adhesives

Protective clothing, gloves and goggles should be worn when handling Hxtal resin and hardener and Loctite 350 since they can all cause severe irritation especially on areas of bruised or cut skin. If skin contact occurs the resin and hardener should be removed by wiping with disposable paper towels and the skin washed in soapy water. If eye conact occurs irrigate with low pressure running water for at least fifteen minutes and seek medical attention..

UV light source

To prevent exposure of the skin on the hands to the UV light source used for curing protective gloves should be worn when aligning and curing joins. UV goggles should be worn when using the light source.

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Harry Clarke and His Geneva Window

by Mary Clerkin Higgins

History

In 1926, the government of the Irish Free State approached one of that country's foremost artists, Harry Clarke, to commission a stained glass window for the offices of the International Labour Conference of the League of Nations in Geneva. Clarke was 36 years old at the time and at the height of his career. He was known internationally for his intense, detailed and imaginative stained glass designs, as well as for his often macabre and bizarre book illustrations. His work, Symbolist in nature, showed a great originality in composition and a masterful use of color.

The Geneva Window (*Figure 1*) was to be an official gift from Ireland to the League. Clarke traveled to Geneva to examine the site and suggested a suitable location in a stairwell. The government left the choice of subject matter to Clarke, who decided upon modern Irish literature, and with the help of friends Lennox Robinson, William Butler Yeats and others, he selected 15 writers and works to illustrate: *The Wayfarer* by Patrick Pearse, *The Story Brought by Brigid* by Lady Gregory, *Saint Joan* by George Bernard Shaw, *Playboy of the Western World* by John Millington Synge, *The Others* by Seumas O'Sullivan, *The Demi-gods* by James Stephens Juno, *The Paycock* by Sean O'Casey, *The Dreamers* by Lennox Robinson, *The Countess Cathleen* by William Butler Yeats, *Mr. Gilhooley* by Liam O'Flaherty, *Deirdre* by George Russell (known as AE), *A Cradle Song* by Padraic Colum, *The Magic Glasses* by George Fitzmaurice, *The Weaver's Grave* by Seumas O'Kelly, and *On Music* by James Joyce.

Work did not begin on the commission until the end of 1927, then progressed very slowly, due to Clarke's numerous other commitments for windows and book illustrations, as well as to the administration of the family stained glass studio and decorating firm. Even worse, Clarke was battling a progressively deteriorating case of tuberculosis. In March, 1929 his doctors insisted that he travel to a sanatorium in Switzerland for convalescence, returning to Dublin over a year later, in May of 1930, to complete work on *The Geneva Window*. It was ready for viewing by September when President Cosgrove of Ireland and other officials came to examine it.

Immediately, President Cosgrove had misgivings. He wrote Clarke, saying that "For several reasons I consider that it would not be desirable to include the panel which contains a representation from the books of Mr. Liam O'Flaherty." His objection to the panel of semi-nude Nelly dancing before Mr. Gilhooley (*Figure 2*) may have been both to the imagery and to the fact that some of O'Flaherty's work was banned at that time by the Censorship Board. His objections grew and he soon wrote Clarke that, "the inclusion of scenes from certain authors as representative of Irish literature and culture would give grave offence to many of our people."

He was hardly alone in that opinion, for as an interview with Mr. R.C. Ferguson, the Secretary of the Department of Industry and Commerce at the time and one of the first officials to view the window, reveals, it was felt by many government officials that "Nakedness was something they we're prepared to accept as an artistic requirement, but never nakedness which so suggested sex.... What harm if this window could be smuggled out to Geneva—but there would be no avoiding the opposition of politicians, churchmen and the newspapers. A nation famed as a Catholic stronghold was to be represented as a bizarre almost viciously evil people steeped in sex and drunkenness and, yes, sin." (*Figures 3, 4, 5*) Politically, there was no possibility that the government would send the window to Geneva.

Harry Clarke, still in fragile health and not disposed to compromise on the window, returned to Switzerland in October, immediately after the viewing, and died there three months later. Officially, the government never said outright that it was abandoning the project; indeed, they paid the agreed sum, in full. However, panels were collected, temporarily went on display, and were then put in storage. Clarke's widow, Margaret, was very unhappy with the commission's outcome and tried in vain either to get the government to send the window to Geneva, which she knew would probably never happen, or to sell it back to her. In 1933, after the installation of a new government, she was allowed to buy the ensemble back for the amount originally paid. The window remained in the family until 1988 and, for part of that time, it was on extended loan to the Hugh Lane Municipal Gallery in Dublin.

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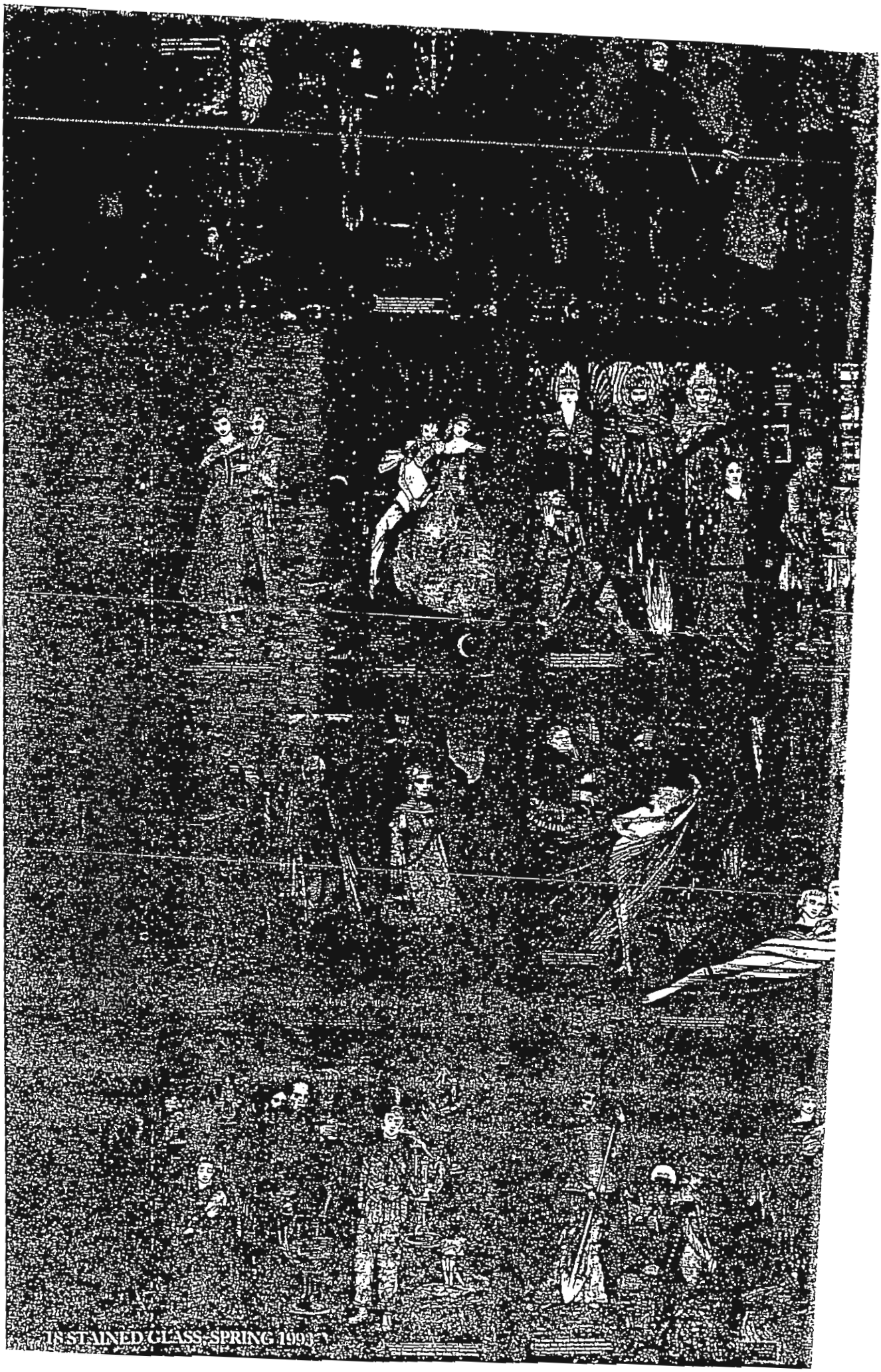

Figure 1: The Geneva Window, *Harry Clarke, 1930, 75" x 41". Before Restoration. The restored window will be unveiled during the Wolfsonian's inaugural exhibition in January 1995.*

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In 1988, the family sold the window to collector Mitchell Wolfson Jr. It is to be on permanent exhibition in the Miami, Florida headquarters of the Wolfsonian Foundation, (*Figure 6*), as soon as construction for the new museum facility is completed in 1995. It will be part of the Foundation's inaugural show, 'The Arts of Reform and Persuasion, 1885–1945.'

While much of the show will travel to sites around the United States, Europe and Japan, *The Geneva Window* will remain in Miami Beach. The Foundation is dedicated to "furthering scholarship, conservation, preservation, education and appreciation of the art and history of the period 1875–1945." As its name suggests, this important and fascinating collection concentrates on the decorative and propaganda arts; that is, art that was not made solely for arts' sake.

As with the rest of the history of this window, its sale was also controversial. By allowing this powerful and historic piece to be purchased and sent overseas, lost to Ireland forever, Brian Fallon remarked in *The Irish Times* that, "We have, quite simply, disgraced ourselves again."

Technique

Although Clarke was not the first to employ the techniques used in *The Geneva Window*, he was a recognized master of them. The entire ensemble is double-plated, with the two pieces of glass held in a single lead, one directly behind the other. Plating is often used to obtain a greater richness and depth of color, or to tone a color. In Clarke's hands, it was used to obtain a much greater variety and intermixture of color.

Most of the glass in the ensemble is flashed. When the glass is still a molten gather, a thin layer of one color is placed over and attached to a thicker layer of another color. This gather is then blown into a cylinder and subsequently flattened into a sheet of glass. Most antique red glass is flashed. Any color however, can be flashed and a whole range of combinations can be achieved,—red over clear, red over blue, blue over yellow, and so forth.

By the fifteenth century, it was realized that a craftsman could remove the layer of flash by abrasion with a sharp tool to reveal the base glass below—a very labor intensive process, enabling the artist to have two colors on one piece of glass without a necessary lead line. In the nineteenth century, hydrofluoric acid was used to remove the layer of flash, making it possible to eliminate all or only a part of the flashed layer, depending on the amount of time the glass was exposed to the acid, as well as allowing for much more subtle and varied tones of color than were possible with abrasion.

Figure 2: 'Mr. Gilhooley,' by Liam O'Flaherty.

(above) Figure 3: 'Deirdre,' by George Russell (known as A.E.)

Figure 4: 'The Others,' by Seumas O'Sullivan.

With *The Geneva Window*, any area that was not to be touched by the acid was protected with a wax resist, while areas to be acided were left uncovered. The glass was either dipped into the wax with some wax then being removed, or hot wax was applied very precisely with a pen. The glass was then placed in a hydrofluoric bath until the proper amount of flash was removed. Clarke would do this as many as six separate times, adding or removing wax resist along the way, in order to obtain many intricate details and various shades of color down to the base, on the one piece of glass.

In the scene from 'Juno and the Paycock' (*Figure 7*) we see the two layers of glass plating side by side. In *Figure 8*, the two layers are stacked as they would be in the leads. Both the front and back layers have been acided and the varying depths of color can be clearly seen. The deepest shade of color was completely protected during the aciding procedure: the clear areas indicate where the flashed layer has been completely removed, revealing the color of the base glass. Aciding with hydrofluoric acid is a very hazardous procedure necessitating a great deal of care and skill, especially for aciding as detailed as this (*Figures 9, 10, 11*).

After the glass was acided, it was painted using silver stain and vitreous paint. The silver stain consists of a silver salt applied to the glass. Upon firing in a kiln, it forms a colloidal

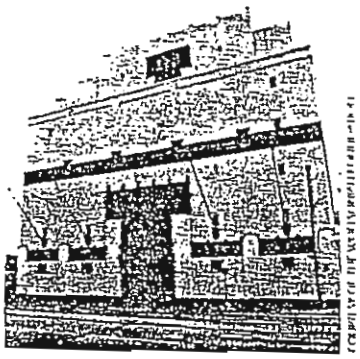
Figure 5: 'The Magic Glasses,' by George Fitzmaurice.

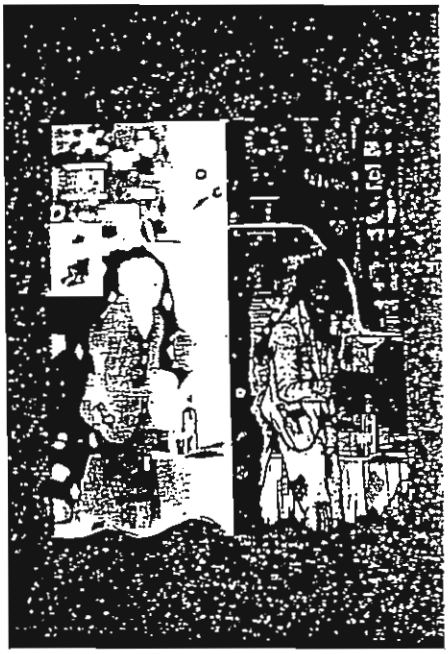
dispersion within the glass, actually staining the glass from a pale yellow to a rich rust color, depending on the amount of silver stain applied, the ability of the base glass to accept the stain and the temperature of the kiln.

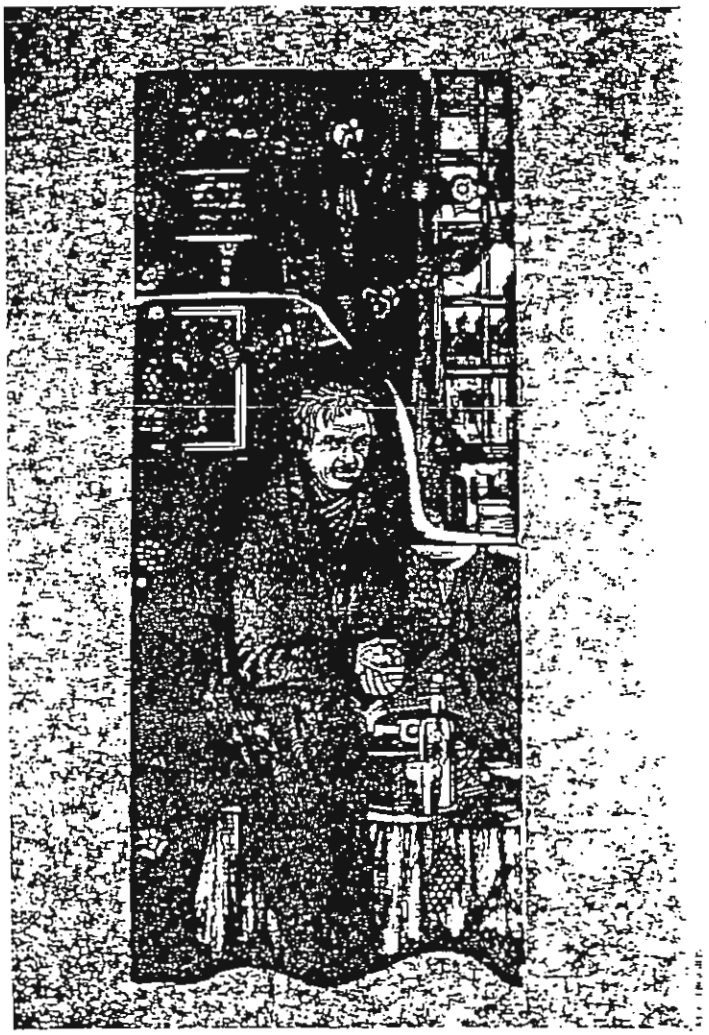
For Clarke, the silver stain meant he could add approximately three shades of yellow to clear areas, plus the mixture of the yellow with whatever his base color was, again increasing his palette. This ingenious use of techniques yielded him a very rich mixture of colors.

Vitreous paint is a mixture of a soft, ground glass flux and metallic oxides. After its application, the glass is fired in a kiln at approximately 1200° F, at which point the soft glass flux fuses to the heat-softened base glass, and holds the metallic oxides in place on the base glass. The vitreous paint was used to add the details and to regulate the amount of light coming through the glass. Clarke employed both a pen and a brush to apply the trace lines. He also used overall mattes, frequently stippled with a stiff brush and worked with a needle. Clarke worked with the vitreous paint much as he did with pen and ink for his illustrations. His painting is very detailed, and by using the pen, he was able to get crisper lines without needing to cut back and straighten, as he would have to do had he used a brush.

Figure 6: The Wolfsonian Foundation Building, Miami Beach, Florida







(left top) Figure 7: 'Juno and the Paycock,' by Sean O'Casey. The two layers of plating, side by side.

Figure 8: 'Juno and the Paycock,' by Sean O'Casey. The two layers of plating, stacked.

Conservation

The most immediate conservation concern was the repair of any new breaks in the glass. With stained glass conservation, there is usually the additional concern of what to do with any previous repairs. The traditional method of repair has been either to cover a break with a lead flange or, more frequently, to insert an 'H' shaped lead came between the pieces of broken glass. This often entailed grozing, or removing some of the original glass to accommodate the thickness of the heart of the lead. Fortunately, none of the breaks in *The Geneva Window* had been grozed. Some cracks were new and had not been addressed, three cracks had been glued with what appeared to be a conservation quality epoxy, and two cracks had been covered at some point, after fabrication, with a lead flange.

There were also a number of original cover flanges on the panels. It was possible to distinguish original cover leads from later ones by their appearance. The originals were done in the same gauge lead as the rest of the panel, and their joints were soldered in the same manner as those on the rest of the lead network.

Glass which has been deeply acid etched and is then painted and fired at a high temperature in a kiln has numerous stresses in it which are sometimes resolved by the glass breaking, either in the kiln or at some later time. It was apparent that a number of pieces broke before the ensemble was finished, and rather than redo the many steps of production in areas where the breaks were not considered intrusive, Clarke decided to simply cover the breaks with flanges. At other times Clarke would redo pieces which had broken in the kiln.

All of the original flanges were left in place. The non-original flanges, however, were removed, because they had not been seen and accepted by Clarke and his assistants (*Figure 12*). Because of the internal stresses from the etching and firing, these pieces had sprung, meaning that they no longer lined up perfectly at the crack, leaving gaps between the two pieces which now had to be filled. This usually does not happen when the glass has been either painted or etched, but the combination of etching and then firing increases the stresses and causes the condition to occur.

Because the pieces were etched, the color fluctuated greatly across the length of the crack and the tinted fill material had to also jump from color to color, as necessary. In this case, the material had to fill, as well as hold, the glass together. HXTAL, a conservation quality epoxy, was used

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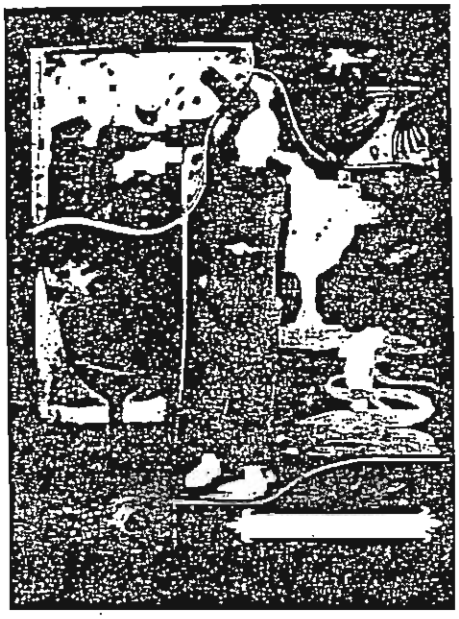
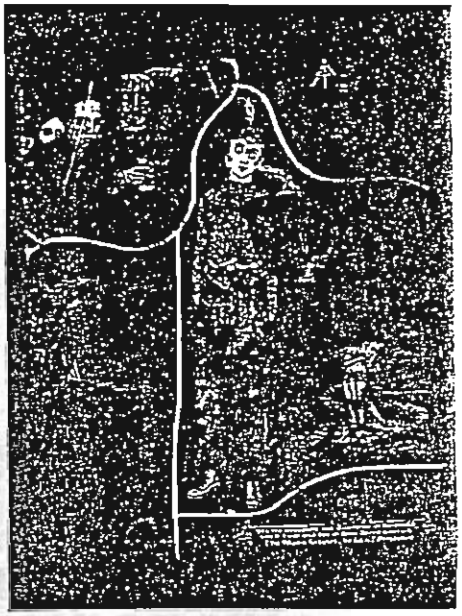
(below left to right)
Figure 9: 'The Magic Glasses,' by George Fitzmaurice. The back layer of plating, etched only.

Figure 10: 'The Magic Glasses,' by George Fitzmaurice. The front layer of plating, etched and painted.

Figure 11: 'The Magic Glasses,' by George Fitzmaurice. The two layers of plating together.





(right) Figure 12: 'The Countess Cathleen,' by William Butler Yeats. Before Gluing.

(far right) Figure 13: 'The Countess Cathleen,' by William Butler Yeats. After gluing and overpainting.

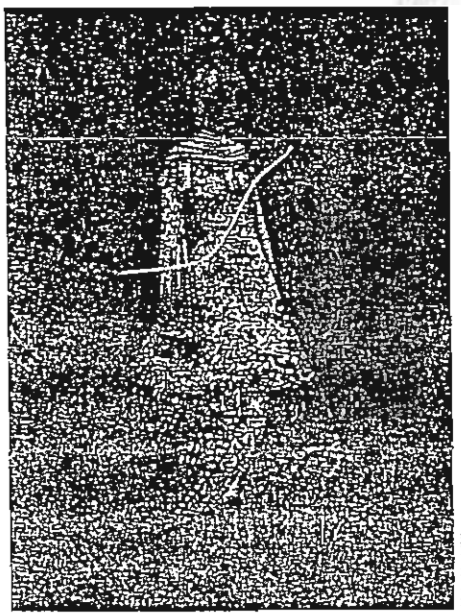


Figure 14: 'On Music,' by James Joyce. After initial gluing.

Figure 15: 'On Music,' by James Joyce. After infill and overpainting.

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for the fills and for any new breaks. It was chosen because it is water-white, has an acceptable match of the refractive index of the stained glass and has held up well in various aging studies of adhesives. The epoxy was then overpainted (*Figure 13*) with cold, or unfired paint, to match the original vitreous paint.

There was one hole in Panel #8, near the head of the minstrel (*Figure 14*), which had been filled in with an opaque brown material. This has now been replaced with a new fill consisting of a thin layer of purple, backed by a thicker layer of lightly tinted HXTAL, to match the flashed purple and tinted glass. The flashed fill was then overpainted to match the original paint (*Figure 15*).

Cleaning was one of the most important steps in the conservation treatment. Clarke's painting technique involved much intricate detailing. Working with a needle, he removed pin pricks of paint through which light would sparkle by halation. Over time, as these filled-in with a film of dirt and, in some places, with an original over-application of putty, the window's glittering appearance was greatly retarded.

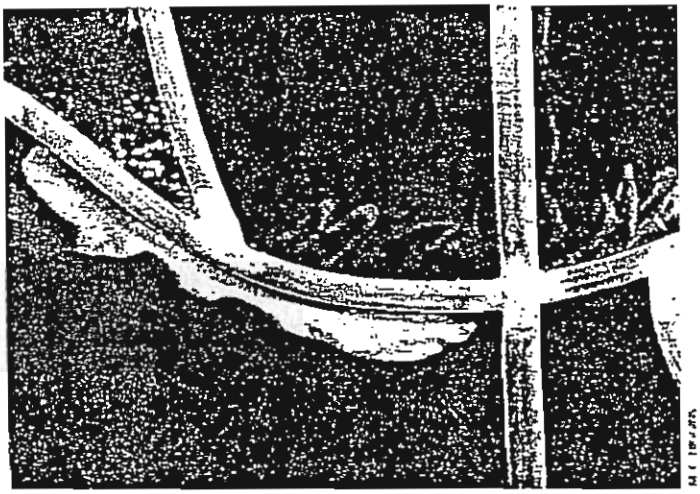
When the glass was removed from its leads for gluing, it became apparent that both the glass and the lead were quite strong and that opening up all of the leads from the back for cleaning would be possible without endangering the glass or damaging the leads. Large drips of original solder were found resting against the glass under the leads; these contributed to some of the breaks in the glass by holding it back in one corner while the rest of the glass could move slightly. These solder drips were removed.

There was quite a lot of dirt adhering to the glass paint on the front surface and trapped between the two layers of glass. When the window was first constructed a linseed oil putty was used to seal the leads. Over time, the putty broke down, allowing dirt and soot to filter in between the layers. A fine film of dirt settled on the two interior glass surfaces, and cut down on the amount of light passing through the glass. Because stained glass is totally reliant on transmitted light, any diminishment of this light will lessen the work of art. As the putty continued to dry out, particles of the putty fell and were trapped between the layers of glass.

All the glass was removed from its leads and cleaned. In this case, because the paint was in excellent condition, the glass was washed using 'Orvus,' a synthetic detergent of Sodium Lauryl Sulfate, then thoroughly rinsed with distilled water. Some additional cleaning was done using scalpels and fiberglass brushes. Once back in the leads, the glass panes were again resealed. All putty oils were completely cleaned off the glass.

When the glass was cleaned, small amounts of wax from the original etching process were found, as well as one instance in Panel #1 in which the medium from the silver stain application had never been removed (*Figure 16*). Since it is a very simple matter to wash off this medium, it was seen as an indication, supported by accounts of the panel's fabri-

Figure 16: 'The Wayfarer,' by Patrick Pearse. The silver stain medium left on the glass.



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cation, of the final rush to complete the ensemble. Analyzed in this light, the remaining medium was of historical interest and left in place on the glass.

The signature is partially covered by the leads. It reads: "Harry Clarke, Dublin 1930."

Conclusion

The sophistication and intricacy of Harry Clarke's stained glass art demand the utmost from the conservator. In order to do simple justice to the panel, the conservator must be conversant in a wide variety of fabrication and conservation techniques, yet must be able to meet the challenges presented with a minimum of ego. In the end, the spirit of the original work of art must be preserved and conveyed to a whole new generation of art lovers and scholars.

The Geneva Window was the last commission Harry Clarke saw completed, and it is certainly one of his masterpieces. The Irish government and powerful religious leaders had banned some of the authors and works represented, most of whom were well respected internationally. The authorities then rejected the visual interpretation of that work, a second act of censorship. Clarke certainly could have expected this, yet he nevertheless proceeded to challenge Ireland's official parochialism. *The Geneva Window* is the work of a mature artist, accomplished in his technique and sure of his vision. In pushing the limits of his craft, as well as the limits of his society's cultural mores, he left us an invaluable legacy and example in his window for the League of Nations. Ω

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MARY CLERKIN HIGGINS, a conservator in private practice in New York City, has worked in stained glass for 17 years. Among her clients are: The Metropolitan Museum of Art, The Cloisters Collection, The Detroit Institute of Arts and The Nelson–Atkins Museum of Art. She conserved *The Geneva Window* for the Wolfsonian Foundation in 1992.

STAINED GLASS CONSERVATION: A FIELD IN FLUX

Mary Clerkin Higgins*

There are often interesting things to be learned from studying the losses in a work of art. Why did they occur? How have they been treated, if at all? What does that tell us about the function of a work and the value placed upon it? While lacunae are an important part of the history of a piece, they can interfere with the aesthetic functioning and appreciation of the work. This paper discusses loss considerations as they relate to stained glass conservation.

Jarrow

At Jarrow in England, fragments of unpainted glass were excavated in 1973 (Cramp 1975). The original method of setting these fragments is uncertain, though a few lead cames (H-shaped lead supports) were also uncovered on the site. Contemporary accounts indicated that window glass at the associated monastery in nearby Monkwearmouth had been leaded together in a glazing undertaken in 675 AD by the Abbot Benedict Biscop and the Jarrow windows may also have been glazed (leaded).

After excavation, the fragments were awkwardly fitted together in a completely conjectural configuration, crudely suggesting a human figure and placed in leads (fig. 1). The result was then put forward, by some, as the "earliest stained glass window."

This "earliest" window would be of great significance if it were true, because, while there are numerous early accounts of colored glass being used to glaze window openings, and several fragments survive, no complete window pre-dates the twelfth century. The edges of this glass are described as being carefully shaped, but the panel makes use of wide leads with significant gaps between the pieces. What we are left with is a group of fragments whose original pattern is not known, that have been placed together to complete some recognizable form.

If one were to accept this configuration of glass and lead, a comparison with comparable objects from the period would suggest that these early artists/craftspeople were not connected with the art of their time, nor were they at all accomplished. While it is very interesting that the fragments exist, it is extremely misleading to present them in their current pattern since what has been put forward would seem to bear no relation to any original configuration of glass or lead. This is an interesting illustration of some of the difficulties faced in the restoration and conservation of stained glass. It is a medium that is made up of discrete parts. Panels can be taken apart, glass can be replaced or re-ordered, and the casual observer may not be at all aware of it, for what they see is, to all appearances, a complete window. The challenge to the

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conservator and art historian is to first discern what has occurred, and then see what is necessary and possible in order to present a window correctly.

An Architectural Art

Stained glass is, traditionally, an architectural medium. In its original location, it is almost always an integral part of the fabric of a building, functioning not only as a work of art, but also as a screen, letting in light and keeping out the elements.

Of the three main components of stained glass - vitreous paint, glass, and lead - the glass and lead are essential structurally, while aesthetically all three play important roles. The loss of any one will impact significantly on the whole. There is not the option of leaving a window in its damaged state on philosophical or aesthetic grounds--a hole exists which must be filled, or soon there will be birds flying around inside the building, as well as light and rain flooding in. The question is not will the hole be filled, but rather, how will the hole be filled.

A variety of methods have been tried over the centuries, but there have proved to be only two reliable, waterproof alternatives in repairing breaks or losses in architectural glass: the replacement of the broken glass, or the insertion of repair leads.

The former means that original material is removed. The latter is unsightly, will begin to confuse the graphic legibility, and may result in glass being cut or ground away ("grozed") along each break line to make room for the insertion of the repair lead (fig. 2).

Modern adhesives have significantly expanded the alternatives, enabling one to achieve effective and unobtrusive repairs both in architectural settings and under museum conditions. Certainly, the function of some windows is purely architectural. They are neither works of art, nor are they historically significant. In these instances it is a matter of general building maintenance and any broken or missing glass would be replaced rather than conserved.

Glass Loss

Glass loss may be attributed to any number of causes -- vandalism, weather (for example, hailstones or hurricanes), various political or religious movements (such as the Reformation and, later, the French Revolution) -- or perhaps to a change in taste.

Restorers frequently take along extra glass (and sometimes glass fragments saved over the years) for emergency repairs on site. Such inserts are intended to be temporary, though they are not always replaced. A "stopgap" is a piece of old glass which is re-used to fill a loss. For example, the head of a figure was found placed backwards and on its side (fig. 3) in an Austrian canopy panel from about 1420 in the collection of The Duke University Museum of Art (1978.20.7). The head was originally from the same group of windows as the canopy, and it is not known when it was inserted here as a stopgap, or what happened to the panel it came from. During the last conservation treatment, the head was removed from the canopy and its gaps were filled where the glass had been grozed with a tinted epoxy resin and then inpainted (fig. 4).

Over time, windows mended using traditional methods can become a jumble of repair leads and glass inserts (fig. 5). While there may be a certain charm to the many insertions in these panels, their arrangement bears almost no resemblance to the original layout. For a number of windows there would be little point, at this stage, in trying to "restore" the glass and lead graphic since so little original material remains.

In Europe, many workshops make use of their glass fragments by piecing them together to fill in windows. The grisaille ensemble, known as *The Five Sisters*, at York Minster Cathedral, England, is composed of many small fragments of glass. It no longer resembles the original grisaille window, which would have had a very definite lead pattern with larger pieces of glass. What is left is actually an assortment of glass fragments which work quite effectively as a large shimmering field of grey.

However, the same approach is much less successful with a figure, and there are many examples of such windows. For instance, in another window at York, a wonderful fifteenth-century head has been glazed together with a body composed of hundreds of fragments of Medieval purple glass and a new border (fig. 6). The artist who created the head would never have drawn such a broken-up figure. While it is understandable that the caretakers would wish to have the head on view, this patchwork approach ultimately does not work since so much is compromised. Glazing together these fragments in this way shows a perfect disregard for the idea behind the original lead pattern. Just as many casual viewers consider it quaint that the Medieval and Renaissance artists drew lead lines across a face (which of course, they did not, as these later leads were used to cover breaks), they will not question this strange assemblage which is the antithesis of the aesthetic pursued by the original artists. Such a fabrication does much more harm than good in fostering an appreciation of the art of stained glass.

In The Field

While there is a growing understanding in the stained glass field of conservation approaches and philosophy, there are still many who would replace original material without a second thought, simply because this is what they have been taught to do in repairing architectural glass.

In one recent instance, a local studio was brought in by museum curators to work on a group of sixteenth-century panels. As the workmen took the glass out of its leads they broke some pieces, yet their attitude was not that they should change their procedures, but rather, that breakage was to be expected and altering their approach would entail a loss of time and money.

Though the conservation department pointed out that they were certainly willing to compensate the studio for the time necessary for a careful job, the workshop maintained that the breakage was not a problem - their glass painter could easily replace the sixteenth-century glass that had broken with newly painted pieces! There was absolutely no understanding of the inappropriateness of this approach.

This relates directly to the purely architectural outlook many studios have. They may not be aware of the conservation issues involved and they only implement the two traditional repair options: the replacement of the glass itself or the insertion of a repair lead. For some architectural glass this might be sufficient, but for much of it, and certainly for any glass in museum collections, this is not appropriate.

In the end, the museum's conservators went to the workshop to glue together the broken glass, since no one there had the skills to do it. The studio still re-leaded the previous breaks just as they found them, rather than eliminating or at least minimizing them. This particular studio's outlook is certainly not unique, but it is also not as pervasive as more and more studios are being exposed to the methods, materials and philosophy of stained glass conservation through articles, workshops, and other means of communication.

Fills

A significant part of any present-day restoration entails determining what glass is original, what has been inserted, and what the original lead lines were. This may involve re-ordering the glass after research and consultation with curators and art historians on the project. Replacement pieces and gaps are usually filled using glass, which is painted, if necessary, with vitreous paints which are then fired in a kiln. These glass inserts are much more stable over time than resin ones would be. They also enable one to better match the missing paint using the original

techniques which may involve the layering of traces, washes and mattes, and brushing and scratching away the dry powdered pigment, all difficult to achieve with "cold" (unfired) paints.

Repairs on glass objects frequently make use of materials which are as transparent or translucent as the glass itself. Resin fills are fashioned to look like the missing area and are attached directly to the original glass. There has been some resistance by stained glass conservators to using this approach, especially when the new fill is of glass. Yet this is exactly what is done in other conservation specialties - a new fill is made, often of the same material used in the original, and joined in a way that is reversible and detectable.

The greatest difference is that glass is translucent and very unforgiving. Because of this, it may not always be appropriate to glue in a fill, but in those situations where it can be done, there is no reason to reject it outright. At times, one may wish to make a clear distinction between original material and later insertions (fig. 7). Here the curator wished to retain the later insertion at the neck of the figure, but not to glue it in. In this instance, the two pieces were copper foiled together.

Glass

The glass itself has many characteristics - color, texture, density, bubbles, striations, to name just a few. While it is not true that Medieval or later glass cannot be duplicated, it is true that it may be difficult or impossible to find in one replacement piece all of the necessary characteristics of the missing glass unless the replacement is custom-made - a very expensive proposition if one can even find a glassmaker to work with who is skilled in blowing and color matching. For the most part, the manufacture of sheets of glass is an industry not tailored to producing small amounts of custom glass.

From the earliest times, stained glass craftspeople have rarely manufactured their own glass. Normally, one group of artisans manufactures the sheets of glass, either hand-blown or machine made, while another transforms the material into stained glass windows. Artists such as Tiffany and La Farge were able to work with small glass factories to produce very unique glass for some of their windows. They passed the considerable cost of this on to their clients. Replacing a glass loss often means going through many dozens of sheets of available glass to find a good match and, as is often necessary, manipulating the replacement with paint or additional layers of glass. Glass may exist that is similar to, but not exactly like the original, which is one compelling reason not to remove original material.

Some losses are due to the composition of the glass itself. In some John La Farge (d.1910) windows, for instance, there are now holes because over time some of the glass developed

numerous cracks which gradually joined together, causing the glass to crumble and fall out of its leads. This particular deterioration cannot be stopped since it is inherent in the glass. The remaining material must be stabilized to prevent more loss and new glass found to match that missing.

Windows composed of more than one layer of glass are said to be plated. One complication in a plated window is that it can sometimes be difficult to know when plating (additional layers of glass) has been eliminated or by whom. The John La Farge window, *Peonies Blown in the Wind* (30.50), made between 1878 and 1881 for Henry Gurdon Marquand's Newport, Rhode Island, residence, and now in the collection of The Metropolitan Museum of Art, had several places where it seemed probable that plating had been removed, since there was still physical evidence on the window of removed plating leads.

One pink cast-glass peony was exceedingly bright and glaring, and from the leads on the back one could see that a piece of plating had been removed. One small petal of the flower still retained its piece of plating behind it. From that petal it was possible to make at least an educated guess that the larger plate had been similar, and then to put on a new plate. In other areas there was no such information, and they were left as they were. It is not known why some of the plating was removed, though there are a number of accounts of plating being taken off American opalescent windows which were considered at some point to be too dark.

Paint

The vitreous paint used on stained glass windows is composed of a low firing glass flux and various metallic oxides, generally iron or copper. After being applied to the glass it is fired in a kiln to approximately 1200° F, at which point the glass flux fuses to the base glass, holding the opaque metallic oxides in place. The paint is used both to control the light and to provide details. Colored glass enamels consist of a lower firing glass flux in which various metallic oxides are either dissolved or held in colloidal suspension, imparting the color. They are usually not as durable as vitreous paints, though the vitreous paint can also fail, due either to a poor composition of the paint, or of the base glass, or to underfiring. Aging and loss are expected, to a certain extent, and have their own aesthetic contributions to make. However, certain losses make a panel very hard to read, at which point one must consider compensating for that loss. The intent is not to make the piece look new, but to make it cohesive where a lack of painted detail is disfiguring. In one panel there may be sufficient information to determine what the missing areas looked like, while in other panels such a determination might be difficult, or impossible.

In a John La Farge panel from the Detroit Institute of Arts (59.170), approximately half of one inscription, "Write me as one that loves his fellowmen," was missing (fig. 8). It was known

precisely what the inscription was and there were still some ghost indications on the glass to guide the layout. A new backing plate of clear glass was cut and painted with the missing half of the inscription. This was fired and then inserted behind the original glass to complete the inscription (fig. 9). The original half of the inscription was then consolidated using Acryloid B72.[1]

Lead

The lead has both a functional and an aesthetic role to play. It is used not only to hold the glass together, but also to relate important information concerning the overall graphic design. These lines are usually planned out by the artist and drawn with great care. Losing the pattern or the scale of the original lead network will significantly detract from the effect of the window. As repair leads are inserted to cover breaks in the glass, the original lead pattern is lost and it becomes very difficult to recognize the iconography.

Lead is, in so many ways, the ideal material to hold the glass pieces together, but it has the disadvantage of needing to be replaced every 100 years or so, due to natural deterioration (eg. cracking and fatiguing). At this critical step it is important that the replacement lead be of the same width and profile as the original so that the scale of the window is not adversely affected and painted details along the edges are not covered or obscured.

The fourteenth-century grisaille panel from St. Ouen, Rouen (fig. 10), in The Cloisters Collection (1984.199.1-11), had been re-leaded at some point with a wide flat lead which altered the scale of the lead pattern to the overall design of the window and also covered important details. A band of yellow silver stain runs parallel to the leads, but this effect was completely lost with the wide replacement leads. In the most recent re-leading this was rectified (fig. 11).

Conclusion

The traditional architectural approaches to the compensation of losses in stained glass windows - glass replacement or the insertion of a repair lead - are still in frequent use but are often at variance with basic conservation principles. Glass compensation is not the only concern, the glass paint and lead came network have their own compensation considerations. While some windows are strictly functional, none would be harmed, and many would benefit substantially, from a greater adherence by craftspeople in the field to the methods and philosophy of conservation.

Bibliography

Cramp, R. 1975. Window Glass from the Monastic Site of Jarrow. *Journal of Glass Studies* (V17): 88-96.

Endnotes

1. Acryloid B-72 is manufactured by Röhm and Haas Company, Philadelphia PA 19105, and is available from Conservation Materials Ltd., 1165 Marietta Way, P.O. Box 2884, Sparks NV 89431, (702) 331-0582.

Figure 1. Map of "conjectural" leadlines. Glass excavated from Jarrow, England.

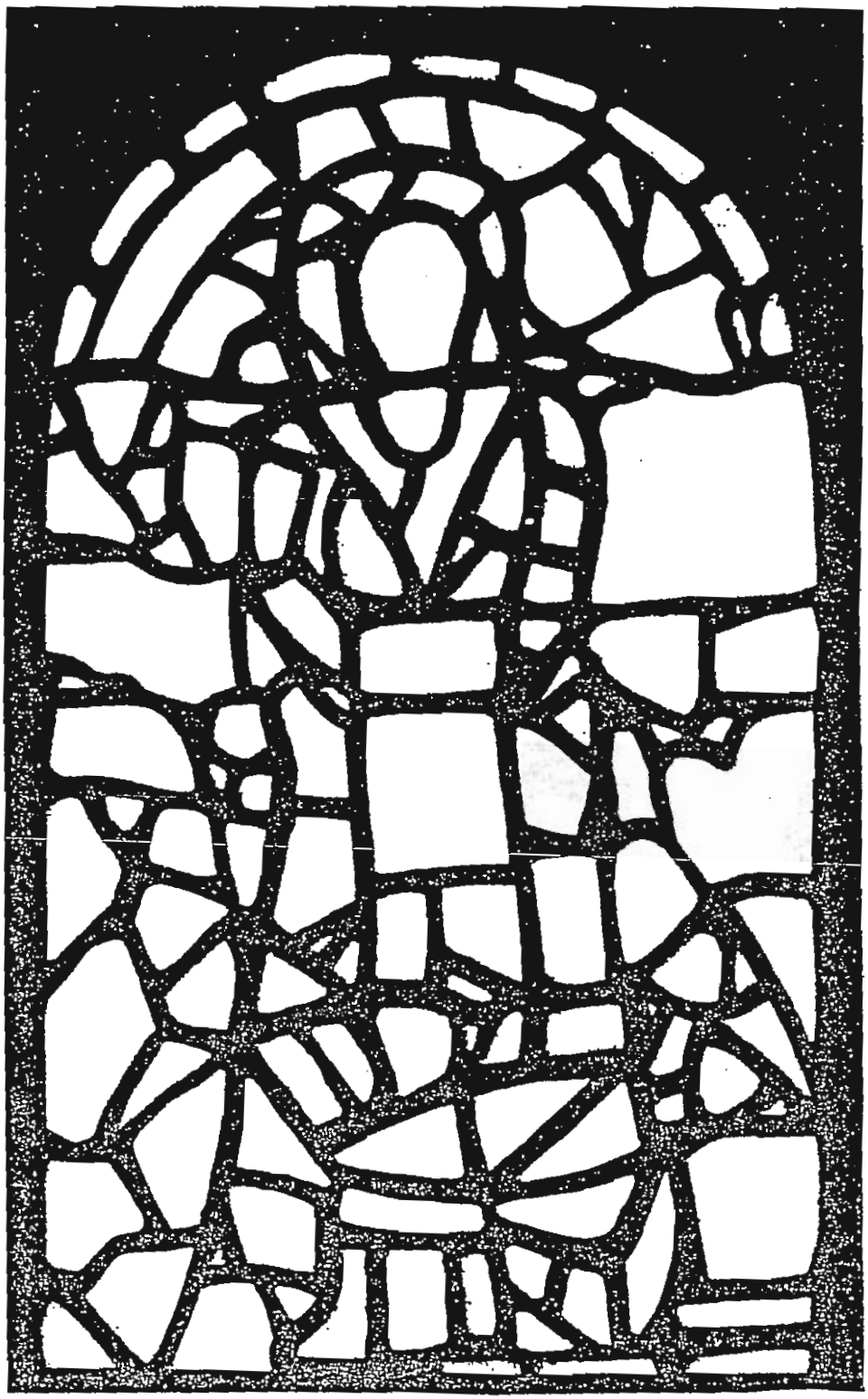

Figure 2. Silver-stained roundel after gap filling, before complete inpainting. The white lines of the fills show how much glass removed after it had broken in order to make room for the insertion of the repair leads. *Ben-Hadid and the Siege of Samaria*, 1525. (MMA, The Cloisters Collection, 32.24.30)

Figure 3. Head of a man inserted on its side and backwards into an architectural canopy section (c.1420), Waasenkirche, Austria. (The Duke University Museum of Art. 1978.20.7)

Figure 4. Inserted head from Figure 3 after cleaning, gluing, filling, and inpainting.

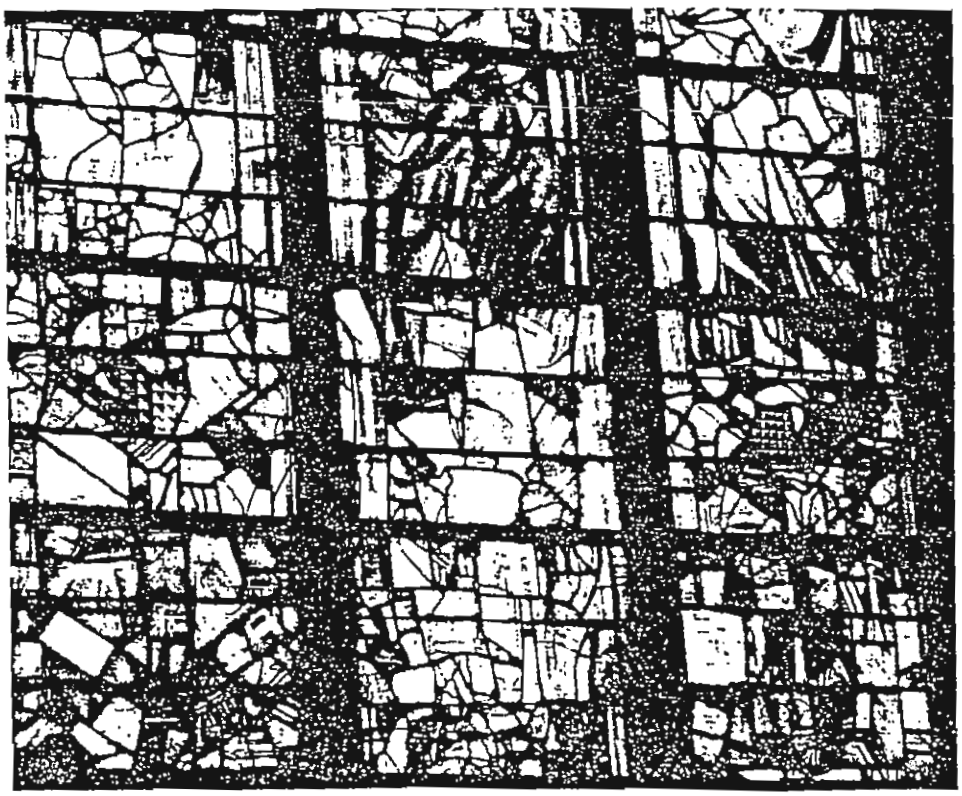

Figure 5. Window made up of glass fragments. Saint Maclou, Rouen, France.

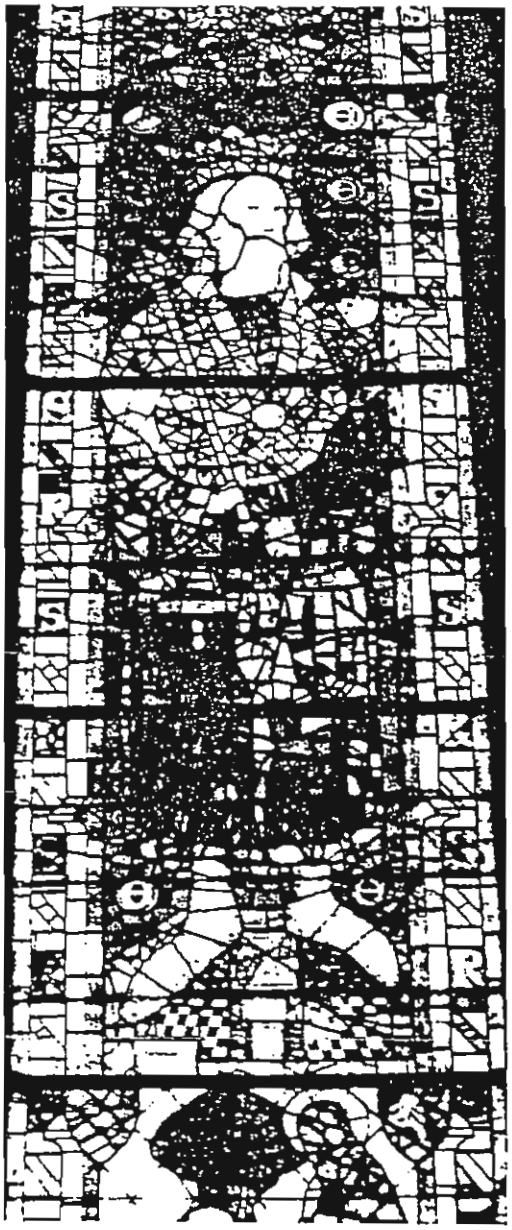

Figure 6. *Edward the Confessor*, York Minster Cathedral, England.

Figure 7. The Virgin's right shoulder is a later replacement. In order to clearly distinguish between the two pieces, they were joined using copper foil rather than an adhesive. *Virgin Kneeling at a Prie-Dieu*; 1552; French. (The Metropolitan Museum of Art, 07.287.12)

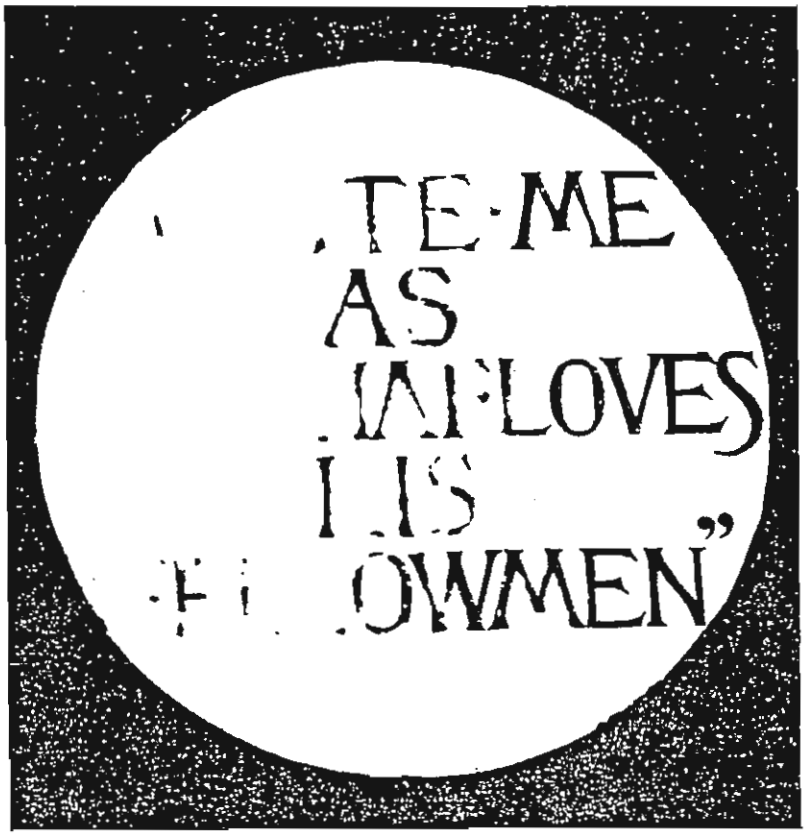

Figure 8. The inscription showing paint loss. *Write Me As One Who Loves His Fellowmen*, John LaFarge; 1889. (The Detroit Institute of Arts, 59.170)

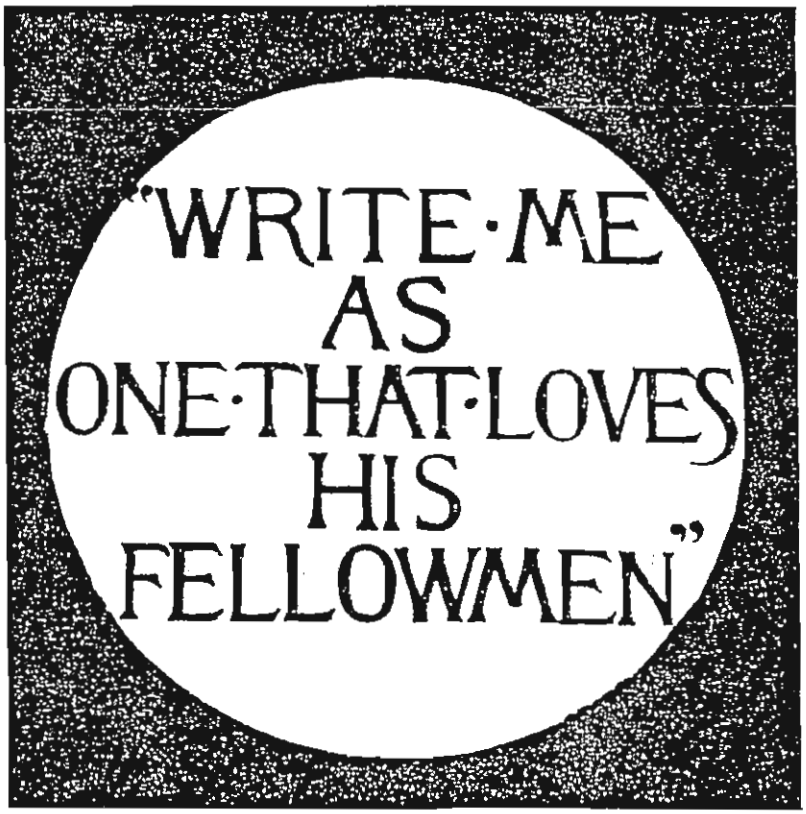

Figure 9. The original inscription together with the backing plate which completes it.

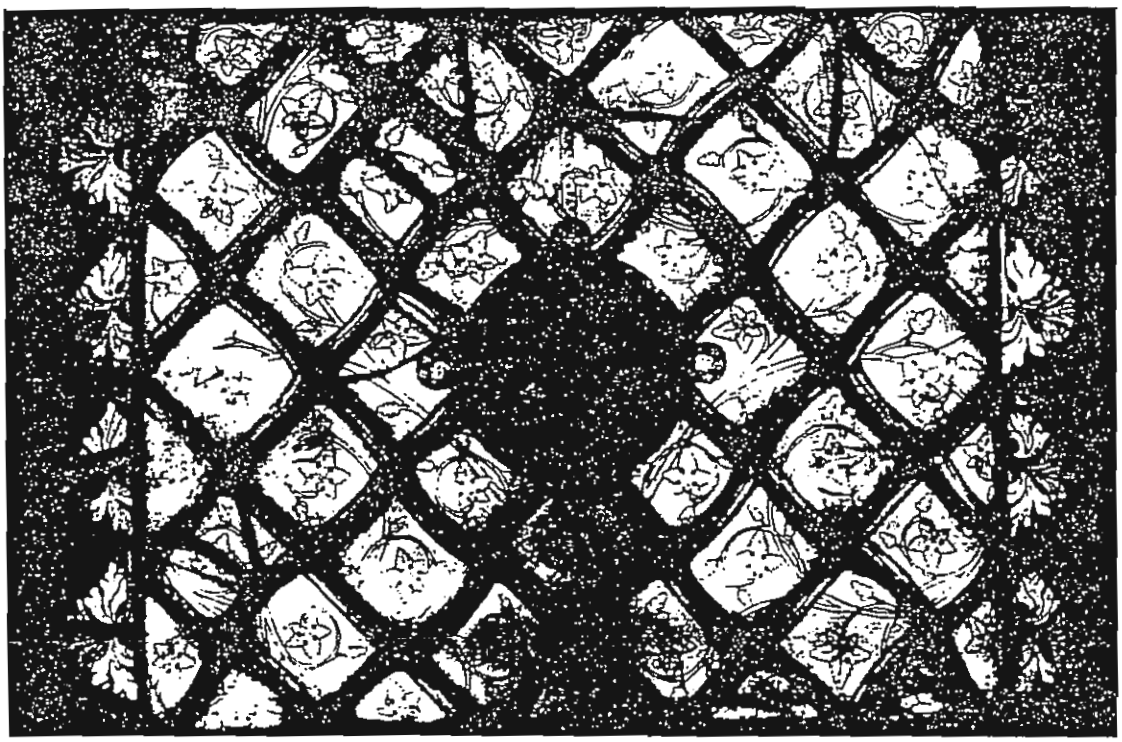

Figure 10. The panel in wide leads before conservation. Note the borders had been attached upside down. Grisaille Panel; 1325; The Abbey of St. Ouen. (MMA, The Cloisters Collection, 1984.199.1-11)

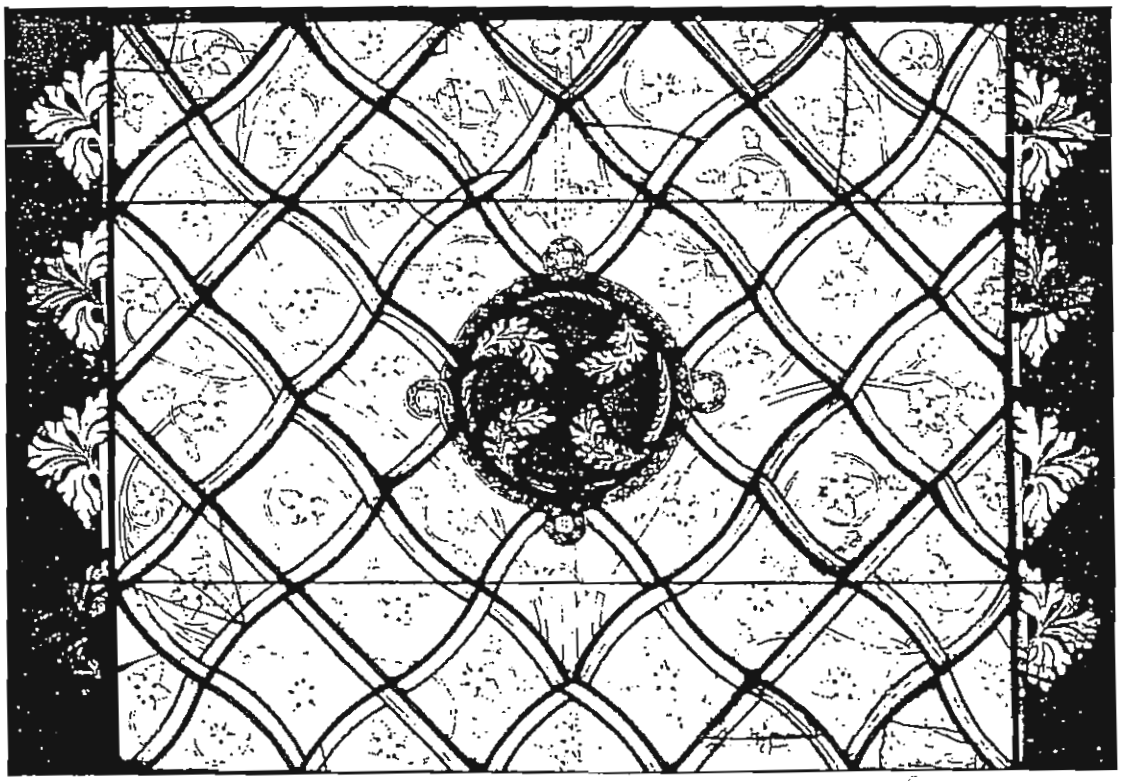

Figure 11. The panel after conservation. It is now possible to see the vitreous and silver stain banding running parallel to the lead lines.

An Unusual Paint on a Silver-Stained Roundel

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The roundel, entitled *Netting Partridge*[1], which you see in the slide on the left, is thought to have been painted in Nuremberg and is dated 1535 to 1545[2]. It depicts a hunter, concealed behind a blind painted with a life-size image of a steer. The hunter herds a covey of partridge through a funnel of low fences into a netted trap. Below the trap, near the edge of the roundel, the head and neck of a fox can be seen emerging from a den. A tree stands prominently in the middle distance, where men and dogs walk in the open area before a village. A castle sits in a hilly landscape in the background.

The design of the roundel derives from a pen and ink drawing by Augustin Hirschvogel (1503-1553) who belonged to a prominent Nuremberger family of stained glass painters.[3] The drawing, which you see in the slide on the right is now in the Museum of Fine Arts in Budapest[4] where it is one of a series of fifty-three hunting scenes by Hirschvogel.[5] Five other roundels based on these drawings have been identified.[6]

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[1]Metropolitan Museum of Art (The Cloisters), accession number 1979.185.

[2]Timothy B. Husband, *Stained Glass before 1700 in American Collections: Silver Stained Roundels and Unipartite Panels*. (*Corpus Vitrearum* Checklist IV). Studies in the History of Art, vol. 39, Monograph Series I (Washington, D.C., 1991) p. 167.

[3]Jane S. Peters, "Early Drawings by Augustin Hirschvogel", *Master Drawings* 17:4 (Winter 1979) p. 359.

[4]Szépmüvésti Múzeum, Budapest, Inventory number (E 19-13A).

[5]Twenty-six of the drawings are in a circular format with a diameter of approximately 23 cm. and twenty-seven are in a rectangular format, measuring approximately 20 by 16 cm.; see Peters, "Early Drawings by Augustin Hirschvogel", pp. 359-392.

[6]Four of these are circular in format and one is rectangular; see Husband, *Stained Glass before 1700 in American Collections: Roundels and Unipartite Panels*, p. 167.

MATERIALS AND TECHNIQUES OF THE ROUNDEL

The glass from which the roundel was cut is transparent and slightly greenish. It contains a few striations and small inclusions, as well as bubbles of various sizes. The bubbles are elongated in lines parallel to the diagonal from about 4 o'clock to 10 o'clock as the roundel is viewed from the front.

The roundel was decorated with various paints and stain applied to both sides of the glass. Vitreous paint in several shades was employed using a variety of techniques. It was applied as a brown matte wash on the front surface to indicate shading. Outlines and details were added with dark trace lines applied over the wash, which was then sticklighted to indicate highlights. This type of paint treatment is apparent in the houses of the village as well as the castle and hills in the background, which you see in the slide on the left. There is also some stipple shading, for example, in the hunter's leg, which you see in the slide on the right. Greyish-brown matte washes of vitreous paint were applied to selected areas on the back of the roundel, which you see in reflected light in the slide on the right. I apologize for the reddish reflection on the glass, which seems to have occurred because of planar distortions in the roundel. Nevertheless, I hope you can see the back-painting on the steer, the partridge, the trunk of the tree, the tree stump in the middle ground, and the lower part of the hill below the castle. In addition, a thin stripe of black vitreous paint surrounds the roundel, covering the grozed edge, as well as extending slightly onto the front and back surfaces. Silver stain was used sparingly. It was applied on the back to color the hunter's cloak, the staves of the fence and the rings of the net, the bird's eyes, and the upper layer of leaves in two of the bushes in the foreground, as well as the bush beneath the tree. A reddish-

orange paint applied on the front surface to color the fox, which you see in the slide on the right, may be sanguine.

The ground cover and foliage, which cover much of the area of the roundel, were colored with a cold paint applied to the front surface . The term "cold paint" is used here to describe an unfired paint and, thus, to distinguish it from a vitreous paint or an enamel, both of which are fired. That the paint was not fired is clear from visual examination under low magnification. It does not exhibit a glassy sheen like a vitreous paint or an enamel and it has developed a craquelure pattern typical of an aged paint film. Where there are losses, the paint has broken cleanly from the glass substrate indicating that there has been no fusion of the two materials. I hope you can get an impression of the appearance of the paint in the slide on the right, which shows a detail of the ground to the right of the tree.

The cold paint is transparent; where it overlays the vitreous paint, the latter is clearly visible through it. This can be seen in the slide on the right where sticklighted matte washes and trace lines of vitreous paint can be seen through the cold paint. The color of the cold paint layer ranges from light amber to brown and is punctuated by discrete areas of green. The larger patches of green are visible to the unaided eye and are mostly located in the middle ground of the landscape, for example, in the ground below the village, around the tree, and behind the hunter. In addition, there are a few spots of green in the foliage of the tree. Under low magnification, smaller spots of green can be seen throughout the cold paint layer.

Despite these color variations, the cold paint layer appears continuous under magnification. Since it was applied to color the ground cover and foliage, it is likely that the original color of the paint was green and that, with the exception of a few isolated areas, it has discolored with age.

GREEN PIGMENTS AND HISTORICAL REFERENCES TO COLD GREEN PAINT ON STAINED GLASS

Before beginning the analytical investigation of the cold paint on the roundel *Netting Partridge*, a review of the green pigments commonly used in the sixteenth century as well as the available documentary evidence for the use of cold green paint on stained glass was undertaken.

Three green pigments were commonly in use in the sixteenth century -- the mineral malachite, which is basic copper carbonate; green earth, a naturally occurring mixture of minerals containing hydrous iron, magnesium, aluminum and potassium silicates; and verdigris, which is a synthetic pigment consisting of either neutral or basic copper acetate, depending on the method of preparation used. When dissolved in a resinous compound, usually with the addition of heat, verdigris forms copper resinate (also known as transparent copper green), which is a transparent green glaze colored by the copper salts of resin acids. The particular resin acid formed depends on the resin used to produce the glaze. Copper resinate was either used directly after its formation, without the addition of any medium, or dried and ground with an oil.

Both verdigris and copper resinate have more intense color and greater transparency than malachite, green earth, or any mixtures of the blue and yellow

pigments known in the sixteenth century. These properties would be important for paints applied to stained glass, making verdigris and copper resinate the more likely choices for this purpose. Both pigments were used extensively on easel paintings during the fifteenth and sixteenth centuries. In the eighteenth and nineteenth centuries other synthetic bright green pigments came into use and the popularity of verdigris and copper resinate diminished. The waning popularity of copper resinate may also have been partly due to its well-known tendency to discolor from green to brown with age. It is generally assumed that the cause of the discoloration is the decomposition of the resinate by ultraviolet light. Where this phenomenon has been noted on easel paintings, the discoloration often occurs only at the surface of the paint layer and is significantly less in areas which have been protected from light exposure.

Thus, a consideration of the properties of the green pigments used in the sixteenth century suggests that verdigris and copper resinate would be the most likely pigments to be used on stained glass. In addition, the apparent discoloration of the cold paint on the roundel *Netting Partridge* appears consistent with the type of deterioration common to copper resinate glazes.

A review of historical treatises dealing with the production of stained glass from the fourteenth through the seventeenth centuries leads to the same conclusion. Among the general discussions of the use of cold paints on stained glass are several references to green paints, specifically to verdigris or copper resinate. For example, the fourteenth century manuscript of Antonio da Pisa states, "If you want to paint on a glass with verdigris and other colors without firing the glass, grind the verdigris or other colors with liquid varnish on a porphyry stone and when you have ground it finely, paint what you want on the glass, and then let it

dry in the sun and it will appear fired. Or truly grind the color with boiled linseed oil and grind it with whichever of these colors that you want. And note that the glass will naturally be a natural green."[7] The second part of this instruction clearly describes the use of verdigris in a linseed oil medium. The first part, however, is less clear. If the term "liquid varnish" refers to a resin, then it describes the preparation of copper resinate by simply grinding the two ingredients together cold, rather then heating them as was the usual practice.

The sixteenth century Marciana Manuscript contains the following directions: "If you wish to paint with other colours which, although beautiful, do not penetrate into the glass, but remain on the surface, especially with verdigris, fine lake, peach-stone black, or charcoal black, and generally all the colours which have no body, and also with fine azure, that is, *ceneri azzurri*, give a coat of nut oil or linseed oil, which last is to be preferred for painting on glass, according the painting which you wish to execute, and let it dry in the shade; then grind up the colour with the same oil, and paint upon the coat of oil and let it dry, and it will be beautiful; and although the color does not penetrate, it will for a long time remain beautiful, and you may even varnish it afterwards, according to the best of your skill ... and when you paint with the verdigris, if you grind some saffron in the same manner with the before-mentioned oil, and with this distemper the verdigris, it will be a green so much the more beautiful...".[8] Again, these instructions describe the use of verdigris in an oil medium.

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[7]Robert Bruck, "Der Tractat des Meisters Antonio von Pisa über die Glasmalerei", *Reportorium für Kunstwissenschaft* 25, p. 240-269.

[8]Mary P. Merrifield, *Original Treatises on the Arts of Painting*, 2 vols., (New York, 1967), vol. 2, pp. 616-618.

There is an additional reference in an early seventeenth century Florentine treatise to the use of a copper resinate type glaze on glass windows. The technique is presented as a "method for making a green to put on glass instead of blinds".[9] The reader is instructed to heat pine resin, mastic, and wax together and then to add verdigris to the hot mixture, stirring until it dissolves. The glaze is meant to be applied hot, that is, immediately after the formation of the copper resinate, rather than letting it dry and grinding it in an oil medium. It is further suggested that to lighten the glaze, turmeric may be added to the mixture.

These excerpts from historical treatises support the idea that verdigris and copper resinate would have been the favored green pigments for use on stained glass.

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[9]G. Birelli, *Opera*, Book 2 (Florence, 1601) quoted in Hermann Kühn, "Verdigris and Copper Resinate" in Ashok Roy, ed., *Artists' Pigments - A Handbook of their History and Characteristics*, 2 vols. (Washington, D.C., National Gallery of Art, 1993), vol. 2, p. 149.

ANALYTICAL INVESTIGATION

Following this historical review, analytical investigation of the cold green paint on the roundel *Netting Partridge* was undertaken. While the characterization and identification of the cold paint is the focus of this study, analysis of the glass and vitreous paint was also performed in order to confirm that these materials were consistent with the sixteenth century dating of the roundel.

ANALYSIS OF THE GLASS

A sample of the glass from the edge of the roundel was quantitatively analyzed using energy dispersive X-ray spectrometry, or EDS.[10] While reported compositions for window glass produced throughout Europe from about the tenth to the fifteenth centuries have generally been of the potash-lime-silica type, with approximately equal proportions of potash and lime[11], the composition of the glass from the roundel, which you see in the slide on the left, has a much higher proportion of lime, with some sodium, and relatively large amounts of magnesium and phosphorus. A similar glass composition was found for seven other silver stained roundels, in the collection of the Metropolitan Museum of Art, from Germany and the South Lowlands, which are dated from the late fifteenth

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[10] The EDS analysis was performed by Mark Wypyski in the Sherman Fairchild Center for Objects Conservation of the Metropolitan Museum of Art. A Kevex model Delta IV energy dispersive X-ray spectrometer attached to an Amray modified model 1100 (1600T) scanning electron microscope (SEM) was used for the analysis. The weight percentages for the glass composition were calculated in comparison with well characterized reference glass. For more information, see: M. Verità, R. Basso, M.T. Wypyski, and R.J. Koestler, "X-Ray Microanalysis of Ancient Glassy Materials: A Comparative Study of Wavelength Dispersive and Energy Dispersive Techniques", *Archaeometry* 36, 2 (1994), pp. 241-251.

[11] See, for example, Ian G. Freestone, "Theophilus and the Composition of Medieval Glass", *Materials Research Society Symposium Proceedings*, vol. 267 (1992) pp. 739-745; and Donald Royce-Roll, "The Colors of Romanesque Stained Glass", *Journal of Glass Studies*, 36 (1994), pp. 71-80.

to the first half of the sixteenth century.[12] The glass compositions of these roundels is shown in the slide on the right. I apologize if the numbers are somewhat difficult to read. Comparable glass compositions have also been published for German glass dating from the fifteenth century and later.[13] The higher proportion of lime in the compositions of these glasses suggests that they may have been made by using an alkali source containing a much higher proportion of lime to potash or by replacing some of the potash or wood ash used in the mix of traditional medieval window glasses with some lime, possibly in the form of chalk. This question is being investigated further by Mark Wypyski. In any case, the details of the composition of the glass from roundel *Netting Partridge* are less important than the fact that it was found to be consistent with that of contemporary glass from the same region.

ANALYSIS OF THE VITREOUS PAINT

EDS analysis of a sample of the vitreous paint from the roundel revealed the presence of lead, silicon and iron, with large amounts of copper and calcium and smaller amounts of aluminum, potassium, and zinc.[14] While the relative proportions of the main components of vitreous paint may vary considerably,[15] this particular composition is not unusual and is similar to the compositions of

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[12]Samples of glass from these roundels were analyzed by Mark Wypyski in the manner described above. The analysis was undertaken as part of the preparation for the exhibition "The Luminous Image: Painted Glass Roundels in the Lowlands, 1480-1560" at the Metropolitan Museum of Art, 28 May - 6 August 1995. The other seven roundels have the following accession numbers: 1985.244, 32.24.43, 1990.119.2, 1985.146, 32.24.67, 1990.119.1, 1982.433.5, 1979.185.

[13]Karl Hans Wedepohl, Ingeborg Krueger, and Gerald Hartmann, "Medieval Lead Glass from Northwestern Europe", *Journal of Glass Studies*, 37 (1995), pp. 65-82.

[14]Data for samples of the vitreous paint and the cold paint (see below) were quantified with Kevex Quantex software using MAGIC IV ZAF corrections for normal standardless EDS analysis.

[15]This observation is based on Mark Wypyski's analysis of vitreous paint on many stained glass panels in the collection of the Metropolitan Museum of Art and does not represent the results of a systematic study.

the vitreous paint on the same group of fifteenth and sixteenth century roundels mentioned earlier.

ANALYSIS OF THE COLD PAINT

The cold paint on the roundel *Netting Partridge* was analyzed by various means in order to characterize it as specifically as possible.

EDS was performed on two samples of the cold paint, one of which was taken from a brown area near the center of the roundel and the second from a green area in the ground behind the hunter. The analyses indicated that both the brown and the green samples contain relatively large amounts of copper and lead, with some calcium, silicon and sulfur, and smaller amounts of other elements.[16] The compositions were found to be unlike the vitreous paint. For example, the cold paint samples contain much less silica and lead and much more copper than the vitreous paint.[17] The high percentage of copper in cold paint suggests that one of the copper-based pigments, such as malachite, verdigris, or copper resinate is present as the major component in the paint. Other green pigments can be eliminated based on negative results. For example, while iron, magnesium, aluminum, and potassium were found, the proportions of these elements were so much lower than that of the copper that it is doubtful that green earth is a major component of the paint.[18]

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[16]The lead found may indicate an intentional addition of lead or it may be due, at least in part, to contamination from the lead came or the vitreous paint, which also contains lead. The calcium may be due partly to contamination from the high calcium glass substrate. The other elements found, such as silicon, phosphorus, and potassium, may be simply the usual inorganic elements found in plant matter, possibly from a plant resin.

[17]In addition, the cold paint samples contain several elements not found in the vitreous paint, including magnesium, phosphorus, sulfur and chlorine.

[18]Eighteenth and nineteenth century green pigments can be eliminated – Scheele's green and emerald green because of the absence of arsenic; viridian and chromium oxide green because of the absence of chromium.

There are some differences in the relative amounts of certain elements in the brown and green paint samples, such as the calcium and the lead. However, the overall compositions are qualitatively very similar and they appear to be essentially the same material. It is possible that the differences in the relative amounts of some of the components may help to explain why some of the green areas have not discolored like the majority of the paint. It is also possible that some of the apparent compositional differences found are due to contamination of the cold paint, for example, by the inadvertant inclusion of some underlying vitreous paint.

A sample of the cold paint was mounted on a glass microscope slide[19] for examination by **polarizing light microscopy**. Under magnification, the paint appears as glassy, irregular yellow fragments with some suspended particulate matter.[20] The particle morphology exhibited by the glassy fragments closely resembles published examples of copper resinate.[21]

The identification of the paint as copper resinate was supported by **Fourier transform infrared spectroscopy**, or **FTIR**.[22] While the typical spectra of verdigris and copper resinate, seen in the slide on the right, are similar, the spectrum of the cold paint from the roundel, seen on the left, corresponds to that of copper resinate.

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[19]The mounting medium used was Aroclor 5442 which has a refractive of 1.66.

[20]The identification of the particulate matter is unclear. It may represent residual material from the initial preparation of the resinate or degradation products.

[21]Kühn, p. 150.

[22]The FTIR analyzis was performed by George Segan Wheeler, Research Chemist, in the Sherman Fairchild Center for Objects Conservation using a BIO-RAD FTS-40 spectrometer. The sample was mounted in a Spectra-Tech diamond cell and placed in a BIO-RAD UMA 500 infrared microscope. The spectrum was collected at four wavenumber resolution with a total of fifty scans.

Since historical recipes for the preparation of copper resinate describe its use either without any additional medium or dried and ground with an oil, **Gas chromatography-mass spectrometry** or **GC-MS** was performed on a sample of the paint from the roundel to determine if any medium is present. The GC-MS gave no indication of the presence of the fatty acids derived from oils. This suggests that the copper resinate was used more or less at the time of its preparation, without the addition of any medium. The possibility exists, however, that an oil medium was present originally but is now so degraded that it is not detectable by this method.

A relatively new analytical technique, which is being evaluated at the Metropolitan Museum of Art for the characterization and identification of a variety of materials is **capillary electrophoresis**, or **CE**.[23] CE is based on the migration of ions through a capillary column subject to an electric field. Its application is suitable for the analysis of the paint from the roundel *Netting Partridge* because, while FTIR revealed the presence of the functional groups of copper resinate, CE could be used to identify the specific resinate. As described earlier, copper resinate can be produced by dissolving verdigris in a variety of resins yielding the copper salts of resin acids. Pine resin, one of the most commonly used resins, yields abietic acid as the principle resin acid. If, therefore, pine resin had been used in the preparation of the copper resinate on the roundel, a peak corresponding to abietic acid would be expected on the

[23]The capillary electrophoresis (CE) analysis was performed by Christopher McGlinchey in the Sherman Fairchild Department of Paintings Conservation of the Metropolitan Museum of Art using a Perkin-Elmer 270A-HT Capillary Electrophoresis System with Turbochrom 4.0 CE data analysis software. Uncoated fused silica columns (Perkin-Elmer) were used and the instrument was operated under normal polarity (i..e., the terminal reservoir electrode as the cathode). The free solution buffer used was 50 mM borate. For further information about this technique, see Christopher McGlinchey, "Capillary Electrophoresis and the Characterization of Some Artists' Materials", forthcoming.

electropherogram of a sample of the paint. However, neither abietic acid nor its common degradation products, whose compounds elute around five minutes, were detected in the CE. This suggests either that pine resin was not used in the preparation of the copper resinate or that the resinate is so degraded that it could not be identified in this way. It is also possible that the unidentified peaks at six, seven, and eight minutes may correspond to uncommon or currently undocumented resin acids or their degradation products. Christopher McGlinchey, Research Chemist in the Department of Paintings Conservation at the Metropolitan Museum of Art, who performed the CE for this investigation, is undertaking further research into the analytical characterization of green glazes. What is interesting about the CE of the cold paint is that a significant amount of acetate ion was detected, suggesting that copper acetate, probably representing unconverted verdigris, is present in the paint. Historical recipes for the preparation of copper resinate are somewhat vague regarding the amounts of the different ingredients to be added. In addition, as Antonio da Pisa's recipe for green paint implied, the mixture may not always have been heated to accelerate the conversion of the verdigris to copper resinate. Therefore, it is not surprising that in a copper resinate paint layer some unreacted verdigris may remain.

CONCLUSIONS

Thus, the analysis performed on samples of the cold paint from the roundel *Netting Partridge*, suggests that it consists of copper resinate and some unconverted verdigris apparently applied without a medium. The use of copper resinate and verdigris on stained glass windows was recorded in several historical treatises and it is not surprising that these intense and transparent pigments were used for this purpose.

The identification of the paint as copper resinate necessitates a reinterpretation of the appearance of the roundel. Although now the foliage and ground cover, which fill much of the composition, appear brown, they would have originally been a vibrant green. In addition, when the roundel was installed in a window, rather than being viewed through a light box as it was for this examination, the unpainted area corresponding to the sky would have been colored a natural blue by the actual sky showing through it. The combination of these effects would be to make the roundel, which now is almost like a *grisaille* in varying shades of brown and black, appear originally as a colorful painting. The slide on the right was digitally color-enhanced to give an impression of what the roundel might have looked like originally. The green color is not entirely accurate and the losses have not been filled, but it gives some idea of the original color balance of the composition.

Much of the recent literature on stained glass technology downplays the past use of cold paints on stained glass, either by omitting any reference to them at all or by relegating their use to a mere corrective device.[24] This view is

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[24]Jean Lafond, *Le Vitrail-Origines, Technique, Destinées* (Lyon, 1988), pp. 68-69.

misleading, especially since the body of historical literature, including those excerpts cited earlier, clearly indicates that cold paints in a variety of colors were applied to stained glass, at least until the widespread use of colored enamels provided a more lasting alternative.

There may be several reasons for the general impression that cold paints were not widely used. One is that existing examples may be overlooked or misidentified. For example, the cold paint on *Netting Partridge* was identified in the *Corpus Vitrearum* Checklist as a "green translucent enamel".[25] This is either a misinterpretation of the nature of the paint or a misuse of the term "enamel", which should be used only to describe a fired paint. More care must be taken in identifying applied colors on stained glass if the full extent of the use of cold paints is to be appreciated. Unfortunately, many examples of cold paints on stained glass may be lost as the cold paint may have been removed from the surface of the glass either through weathering or from misguided cleaning. Giorgio Vasari, writing in the second half of the sixteenth century, refers to this phenomenon when he describes the advantage of the more permanent enamel paints: "In this art the Flemings and the French have succeeded better than the other nations, seeing that they, with their cunning researches into pigments and the action upon them of fire, have managed to burn in the colours that are put on the glass, so that wind, air, and rain may do them no injury, whereas formerly it was customary to paint windows in colours coated with gum and other temperas that wasted away through time and were carried off by the winds, mists, and rains, till nothing was left but the mere colour of the glass."[26]

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[25]Timothy B. Husband, *Stained Glasss before 1700 in American Collections: Silver-Stained Roundels and Unipartite Panels*, p 167.
[26]Giorgio Vasari, *Vasari on Technique*, trans. Louisa S. Maclehose (New York, 1960), p. 267.

This presentation was originally entitled an "unusual" paint on a silver-stained roundel. However, perhaps the term "unusual" is incorrect. Today we have seen and heard of many examples of cold paints on stained glass. Hopefully, as a result, we will all become more aware of the existence of cold paints and more attentive to their proper identification and preservation.

ACKNOWLEDGEMENTS

In closing, we would like to thank our colleagues at the Metropolitan Museum of Art who contributed to our research: Timothy Husband, for allowing us to examine the roundel; George Segan Wheeler for performing the FTIR and GC-MS analyses; Christopher McGlinchey for performing the CE analysis; and Paul Caro for the computer graphics. And thank you for your attention.

EDS ANALYSIS OF VITREOUS PAINT FROM ROUNDEL
NETTING PARTRIDGE (MMA 1979.185)

Weight %	Vitreous Paint
Mg	nd
Al	1.3
Si	13.4
P	nd
S	nd
Cl	nd
K	0.8
Ca	6.2
Fe	14.3
Cu	8.5
Zn	1.7
PbO	53.7

EDS ANALYSIS OF GLASS FROM SILVER-STAINED ROUNDELS

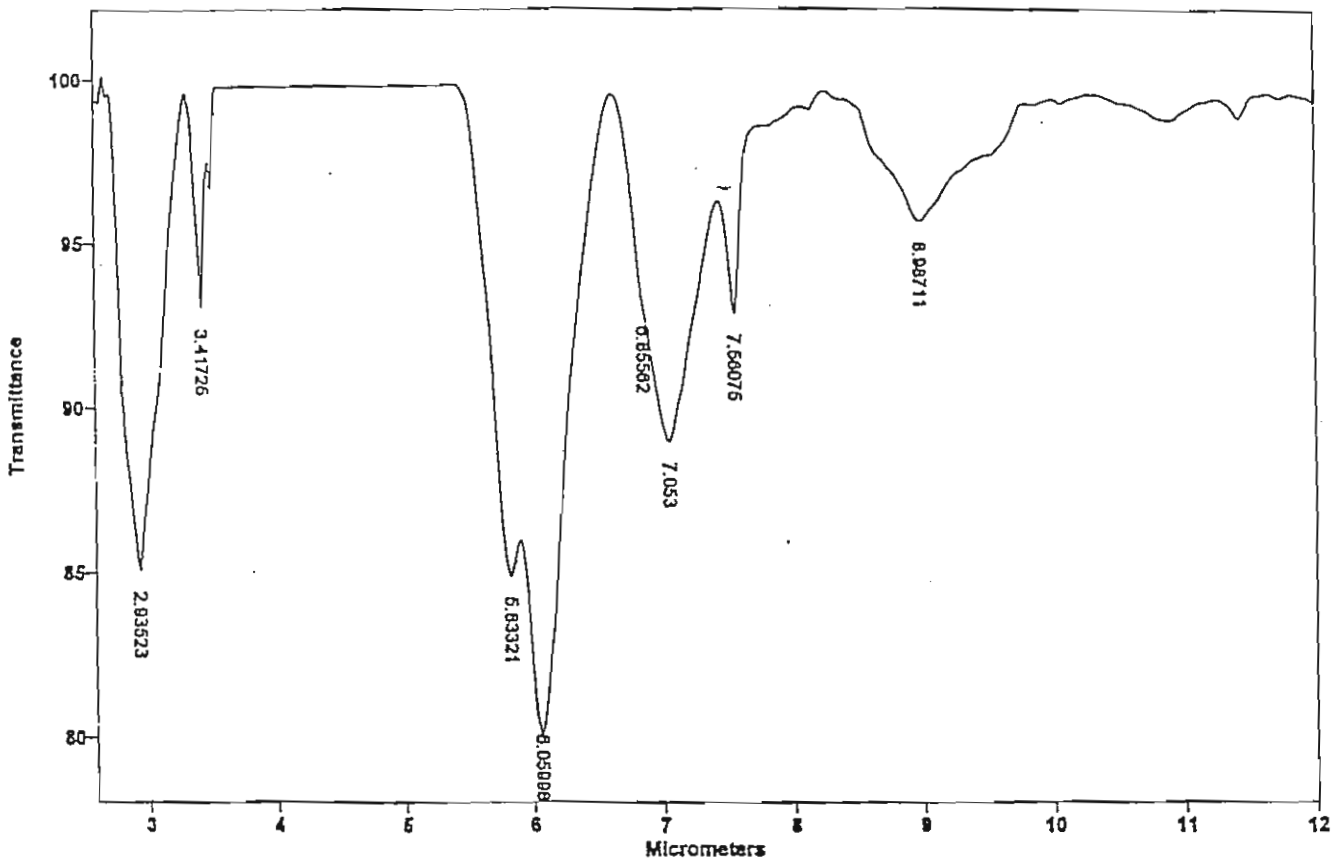
wt. %

No.	MMA Acc. No.	Date	Provenance	Na2O	MgO	Al2O3	SiO2	P2O3	SO3	Cl	K2O	CaO	TiO2	MnO	Fe2O3	CoO	BaO
1	1985.244	1480-1500	S. Germany	0.9	3.5	5.4	58.9	2.1		0.1	8.3	19.2	0.2	0.7	0.9		0.4
			(Blue Border)	2.7	3.6	2.7	56.7	3.4	0.2	0.4	5.7	22.8	0.2	0.8	1.0	0.1	0.3
2	32.24.43	1500-1510	S. Lowlands	2.3	2.9	2.7	58.6	3.3		0.5	5.2	22.4	0.1	0.6	0.5		0.2
3	1990.119.2	1500-1510	S. Lowlands	2.6	2.6	3.2	60.3	3.2		0.6	4.9	21.1	0.1	0.5	0.5		0.2
4	1985.146	1507-1515	Nuremberg	0.9	3.4	3.3	60.1	1.9		0.1	8.4	19.8	0.2	0.9	0.6		0.6
5	32.24.67	1515-1520	S. Germany	2.5	3.5	3.5	58.8	2.5		0.6	5.1	21.1	0.2	0.5	0.6		
6	1990.119.1	ca. 1520	S. Lowlands	2.3	2.9	3.4	61.5	2.8		0.5	5.2	20.6	0.1	0.6	0.6		0.3
			(Clear Border)	2.6	3.7	3.1	59.6	2.9		0.7	4.1	21.6	0.1	0.5	0.5		0.2
7	1982.433.5	1532	S. Germany	2.9	3.3	6	55.5	2	0.2	0.5	4.9	22.7	0.2	0.5	0.8		0.5
8	1979.185	1535-1545	Nuremberg	2.4	3.5	3.1	55.5	3.6	0.2	0.6	6.2	23.1	0.1	0.6	0.5		

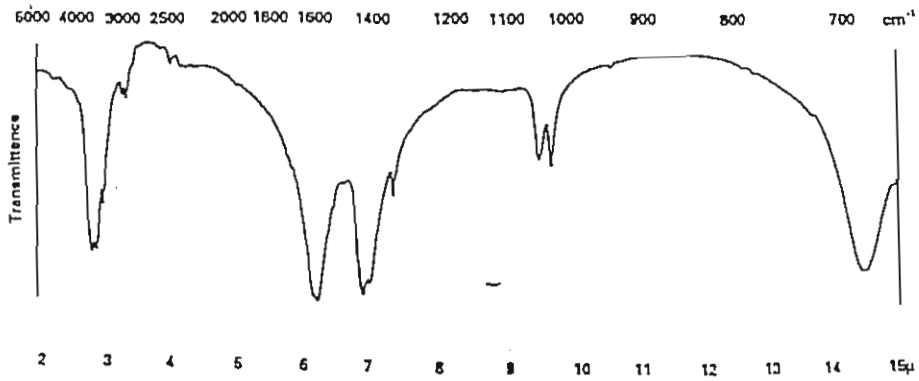
EDS ANALYSIS OF COLD PAINT FROM ROUNDEL
NETTING PARTRIDGE (MMA 1979.185)

Weight %	Brown	Green
Mg	1.8	0.8
Al	4.7	2.4
Si	7.1	4.8
P	0.2	0.5
S	7.6	3.5
Cl	3.1	0.9
K	3.9	1.6
Ca	11.4	20.3
Fe	2.6	2.1
Cu	40.4	25.2
Zn	0.9	0.5
PbO	16.4	37.4

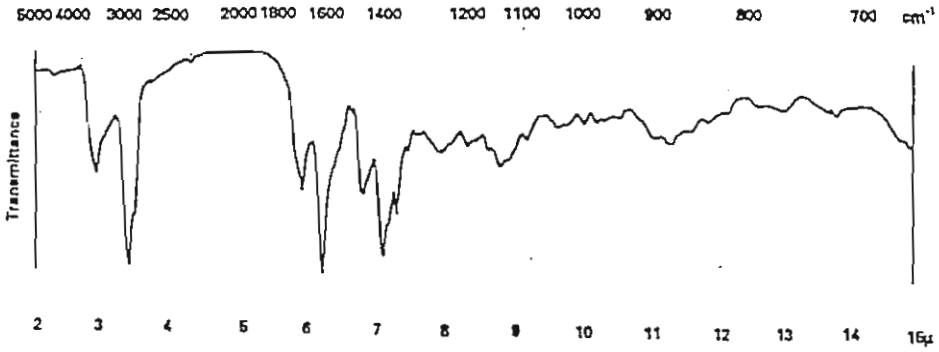
FTIR SPECTRUM OF COLD PAINT FROM ROUNDEL NETTING PARTRIDGE (MMA 1979.185)



IR SPECTRA OF VERDIGRIS AND COPPER RESINATE
(Adapted from Kühn)

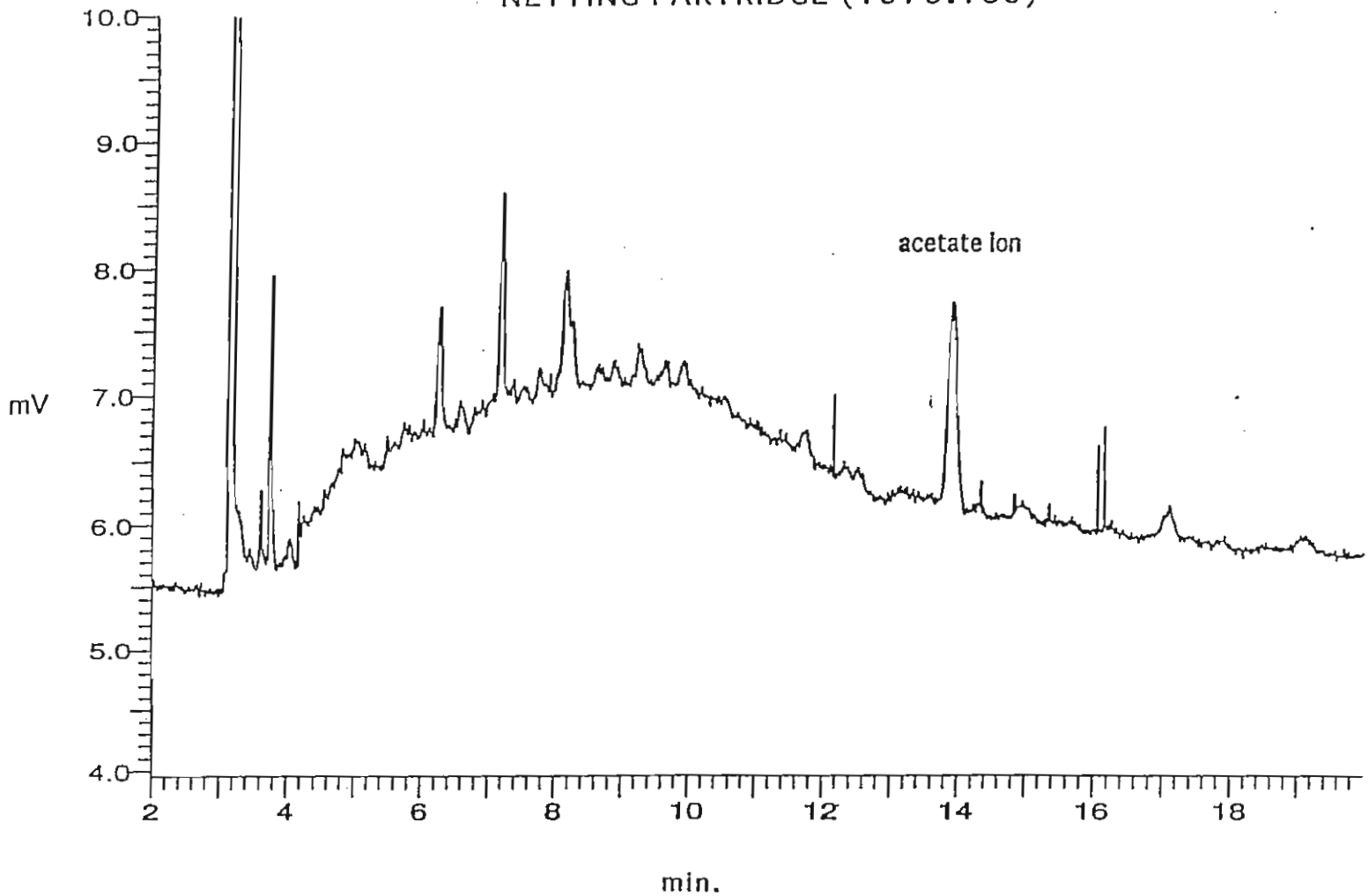


neutral verdigris without medium



commercially available copper resinate

CAPILLARY ELECTROPHORESIS OF COLD PAINT FROM ROUNDEL NETTING PARTRIDGE (1979.185)



EDS ANALYSIS OF GLASS FROM ROUNDEL
NETTING PARTRIDGE (MMA 1979.185)

Weight %	Glass
Na_2O	2.4
MgO	3.5
Al_2O_3	3.1
SiO_2	55.5
P_2O_5	3.6
SO_3	0.2
Cl	0.6
K_2O	6.2
CaO	23.1
TiO_2	0.1
MnO	0.6
Fe_2O_3	0.5

Windows in Religious Buildings:

HIGHER STANDARDS NEEDED FOR PROTECTIVE GLAZING

Installation of protective glazing is very popular on religious buildings for storm protection and security. However, a recent study shows that improperly designed secondary glazing can cause more problems than it cures.

BY NEAL VOGEL, *Inspired Partnerships, Chicago, Ill.*

The vast majority of U.S. churches have protective glazing (PG) today, yet a recent study proves that it causes serious damage to stained-glass windows nationwide by increasing condensation and heat build-up in the airspace, and preventing routine maintenance. As part of an initial investigation of protective glazing issues, Inspired Partnerships performed a field survey of 100 PG installations nationwide. Condensation was found in 70% of the windows. Nearly all plastic glazing (over 60%) had clouded over, while some of the windows were too obscured to see through at all. Only 4% of the PG installations were intentionally vented while another 19% self-vented due to deteriorated sealants or broken glazing. Despite recorded heat and condensation problems, most of the stained and painted glass was in good condition overall, but the leading, bracing, and window frames were severely deteriorating in many windows. PG also prevents routine window maintenance. Approximately one-third of the windows surveyed required maintenance to the frames that were no longer accessible due to fixed storm glazing. For historic churches and synagogues, plastics (acrylics and polycarbonates) in particular have become the vinyl siding problem of windows. The Protective Glazing Study calls for higher standards in the glazing industry to address the current problems with PG materials and installations, and to employ PG only when necessary.

Promotion and Use of Protective Glazing

The ever-changing face of religion, architecture, art, and the economy since the 1950s has resulted in greater competition for fewer stained-glass installations. In order to stay in business, many contractors fully endorse PG, which is a lucrative aspect of the glazing industry. Brochures collected since the 1960s reveal that most contractors use at least some of the following reasons to promote PG to consumers: vandalism, security, energy, comfort, conservation, weather, sound, and maintenance. Civil unrest during the 1960s motivated a number of congregations to cover their stained-glass windows with PG for vandalism protection. Fear over vandalism and theft, whether justified or not, remains a powerful motivator for PG, especially in the inner-cities.

The 1973 energy crisis further convinced many misinformed churches that secondary glazing was a worthwhile investment to reduce fuel bills. Today, energy savings remains among the three most popular ways to promote protective glazing, along with vandalism and storm protection. However, testing for the study demonstrates that the perceived energy value is a myth for intermittently occupied buildings (e.g. churches, synagogues). The results show that the energy savings from properly vented protective glazing has a very slow payback of more than four decades in the continental U.S. and does not warrant the expense of installation.

Perhaps more important than fear of vandalism or energy concerns is the financial inability of many congregations to fund stained-glass restoration. Many dwindling congregations faced with the reality of restoration costs choose to defer the expense by burying their window problems temporarily with PG. Regardless of the aesthetic or conservation impact on stained glass, PG stops leaks and drafts through deteriorated windows and postpones the inevitable restoration costs. Procrastination has been the decision of thousands of congregations nationwide, and today about 80% of U.S. churches with stained glass have some type of PG. But in recent years, a stronger sense of stewardship, intensified professional criticism of PG, and a swelling restoration market is prompting the question, "Do we need protective glazing...or do we really need restoration?" *(For a discussion of stained glass restoration, see the article on p. 56. — Ed.)*

Aesthetics

Although the glazing industry has claimed many advantages for PG, no one has claimed that it improves aesthetics. Windows that are not covered with PG look the best (Figs. 1 & 2). The design, materials, and installation of secondary glazing can have a serious aesthetic impact on stained-glass windows and historic buildings. The exterior appearance of stained glass is often as important as its interior appearance — particularly in ecclesiastical architecture. Virtually all Gothic style churches rely on pointed-arched window frames and delicate window tracery to accentuate the vertical design. When a conventional grid is installed over the original frame, the building's architectural character is severely compromised (Fig. 3).

Most glass products today are very stable and will retain excellent clarity over the years. However, it is important to consider how light will play off the glass surface; reflections are disconcerting when PG is viewed on an angle. Some PG systems employ leading to break up the broad expanse of sheeting and mitigate the glare. On primary facades, and where leading and texture are of great importance to the perception of the building, this is a worthwhile approach. Plastics are also susceptible to glare, but worse, they become cloudy (nearly opaque) over time. Manufacturers recognize this chronic problem and do not warranty their products beyond a few years. Aesthetically, all plastic products are a poor investment and their initial appearance will certainly decline in a relatively short period of time.

The design of the PG framework should be compatible with the design, materials, and color of the original stained-glass window frame. Installations in which the glazing is cut to fit within the existing tracery are visually most successful. An advantage of wood and steel frames is that they can be painted to match or complement the original frame. Select materials carefully to enhance the windows and architecture.

Maintenance

The most common result of an improper PG installation is condensation. Owners of religious buildings are notorious for neglecting maintenance, particularly on high windows; paints and sealants nearly always fail before they are renewed, causing leaks into (often) unvented PG. Moisture, which promotes glass corrosion, gets trapped between the glazing, and condenses on the stained glass, PG, framing members, and window surround.

Protective glazing is often promoted to alleviate window maintenance. Unfortunately, it is typically installed in a fixed position, becoming a *barrier* to window maintenance. If sealant integrity is maintained on a newly restored window, condensation may not occur for a while. Soon, however, weathering deteriorates paints and sealants, and excessive moisture inevitably occurs. Moreover, PG imparts a false sense of security so routine window maintenance is often overlooked as a property management responsibility. Even if failing paint and deteriorating wood are apparent, building owners are reluctant to remove PG due to the significant cost.

Frame problems concealed behind cloudy secondary glazing are "out of sight, out of mind" and neglected. Wood windows are particularly at risk as laminations and joinery readily admit water once the paint and sealants fail (Fig 4). Iron frames rust more quickly under humid conditions, which can deform glass and crack masonry; severe rusting can necessitate entire frame replacement. While stone tracery is generally more tolerant of improperly installed PG, damage often occurs from inappropriate sealants and anchors. Frequently, PG is mounted against masonry with fasteners that rust — staining and spalling the masonry. Unvented protective glazing also has a "greenhouse effect" on the airspace between the stained glass and secondary glazing. In the U.S., this effect occurs on unshaded east, west and south elevations. An unvented airspace can be subjected to high temperatures, measured up to 165°F, as solar radiation is absorbed throughout the day. Perhaps more critical than temperature peaks are the exaggerated temperature fluctuations in an unvented PG airspace; one unvented PG airspace swung 90°F over a 24-hour period!

These exaggerated temperature swings augment the expansion and contraction cycle of the lead came holding the glass together. Lead has a high coefficient of thermal expansion and a low modulus of elasticity. The expansion-contraction of lead came from thermal change is approximately three times that of steel, four times glass, and seven times wood (typical adjacent materials). As it heats up, lead came expands along its length, but it does not rebound when it cools. The pressure generated by this continuous expansion causes stained glass to buckle and bow out of plane. Research indicates that if a leaded-glass panel is going to deform, it will deform more rapidly when exposed to higher temperatures; deformation occurs twice as fast at 120°F than at 70°F.

Protective glazing (PG) is defined here as a secondary layer of glass or plastic on the exterior of a stained glass window; it is also described as storm, double, outer and secondary glazing throughout this article. Stained glass pertains to all types of leaded glass.

Many American windows are having deformation problems that seem related to heat build-up in unvented PG installations. Although imported, plated, and high-end windows show few signs of heat-related deterioration, low-end art glass or "catalog" windows (particularly those fabricated with narrow 1/8" came) appear to be more seriously affected by heat build-up. New, or recently re-leaded windows installed with unvented PG are at the greatest risk. These supertight installations produce the highest temperatures. Therefore, deformation is accelerated on the front end of the window's life, which is the least desirable effect. The service life of a stained-glass window, at least one that is susceptible to deformation, can be reduced by years due to unvented PG.

continued on page 130

PROTECTIVE GLAZING, continued from page 86

Unfortunately, this process occurs over many years and is difficult to document under actual weathering conditions.

Secondary glazing frequently prevents normal window operation as well. Almost all churches require some ventilation during various seasons, and permanently mounted secondary glazing often immobilizes ventilators. Sometimes building owners look to more expensive alternatives, such as central air conditioning, to solve ventilation and comfort problems.

Light & Sound Transmission

All secondary glazing reduces natural light through stained glass. For most types of glass, the light reduction is insignificant. Clear, clean, polished glass reduces light transmission only 3%, while clear, clean Lexan reduces light transmission about 16%. However, when dirt collects on the inside surface of the PG, and when plastics become cloudy, light can be dramatically reduced. Removing or replacing old PG with clean glass can increase light transmission over 100%. All secondary glazing, whether plastic or glass, reduces sound transmission through stained glass. This can be beneficial when excessive urban or industrial noise is present. Laminated glass, particularly laminated insulating glass, is the best choice in reducing sound transmission. True sound reduction also varies depending upon the depth of the airspace — the deeper, the better. Under normal circumstances, though, the sound transmission is only reduced a negligible 5-15% with protective glazing.

Installation Guidelines for Protective Glazing

It is better *not* to apply protective glazing than to apply it improperly. However, there are instances where recurrent vandalism, stained-glass conditions, or stained-glass value warrants a protective glazing system. Conservation of the stained glass itself should be the overriding consideration for any PG installation. Isothermal protective glazing, where the stained glass is remounted on the inside of insulated glass and the airspace is vented, is the best method in many instances for stained-glass conservation. Isothermal glazing guarantees that no condensation will occur on the interior surface of the stained glass, which is a primary concern when unstable paint conditions are apparent. However, isothermal systems are expensive, require careful design, and are not necessary for most stained-glass windows in America. When designing PG installation details, the following issues must be considered:

1. *Framework Configuration:* Successful PG installations mimic the shape of the tracery or mullions that support the stained glass.

2. *Texture, Leading & Frame Color:* For buildings where the glass texture, leading pattern, or exterior color (opalescent glass) are important to the architectural design, large sheets of PG are an unacceptable compromise.

3. *Depth of Window Opening:* Installations that maintain a reasonable setback and engage window moldings and tracery, rather than covering them, look better.

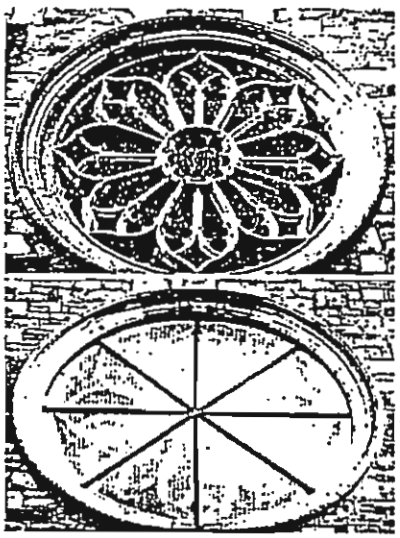
4. *Glazing Attachment Method:* PG should never be attached directly to the existing frame, but rather attached and securely anchored within the frame surrounding the stained glass. Glazing should be placed within sashes or reglets to allow for expansion/contraction, and all fasteners should be nonferrous.

5. *Frame Material:* Frame components should be fabricated of the same material (either metal or wood) as the original window surround. Bronze or anodized aluminum may be acceptable, but mild steel will rust and should not be used. In coastal areas, special coatings or alloys may be required to avoid corrosion.

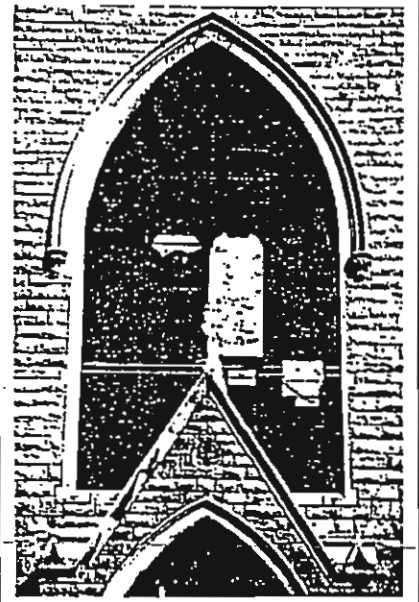
6. *Glazing Material:* Laminated glass is recommended in most instances due to its durability, resistance to breakage, and stable clarity.

7. *Venting:* The airspace formed by protective glazing must always be vented.

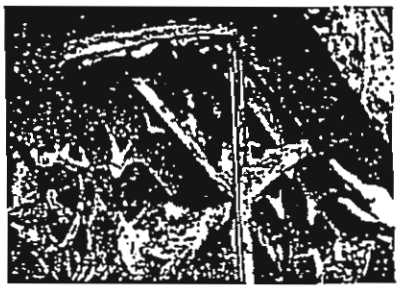
There are three primary reasons for venting PG: (1) to allow condensation to evaporate; (2) to equalize the pressure in the airspace with the atmosphere; and (3) to minimize the temperature variation in the airspace. Where and how the glazing is vented depends on the type of installation and the climate. In a northern temperate climate, the airspace should generally be vented to the exterior of the building. In a hot, humid climate, venting to the interior should be considered if the building is air-conditioned throughout most of the year. The venting needs of particular windows may vary greatly. The amount of venting required is dependent on the micro-environment that the window is subject to, based on climate, orientation, and the depth of the airspace.



The delicate tracery of this rose window, a dominant exterior architectural feature, was totally obliterated by this insensitive protective glazing.



The grid of protective glazing applied over this lancet window prevented vandalism, but also destroyed the character of the window.



The decay visible in the wood tracery and window frame reveals an extreme case of the type of damage that can be caused by improperly installed secondary glazing.

If applied frames are used to support the PG, holes can be drilled through the frame to allow for air movement. The holes must be at the top and bottom of the window and be designed to keep out rain and insects. If plastic glazing is used, the holes can be drilled through the plastic in similar fashion. If the exterior glazing is leaded, vents (stainless steel screens) can be glazed into the window during fabrication. If glass is used, the corners can be cut off and fitted with a hooded vent screen comprised of glass, stainless steel screening, and lead came. The openings should only occur at the top and bottom to cause upward airflow through the airspace (i.e. "chimney effect").

Exact specifications as to the amount of venting do not yet exist, but it is clear that the best system is one that can be easily modified to allow for greater or lesser airflow. In-situ experimentation remains the best way to determine proper venting. PG installations should be monitored throughout the year for evidence of condensation, such as moisture trails (faint streaks from drips) on the interior surface of the stained glass or PG.

Wire screens are often a good alternative to glazing materials and are gaining favor, particularly in Europe. They are an effective, and often inexpensive, impediment to vandalism and impact damage to stained-glass windows. They also provide some security and allow for periodic rinsing of the windows on the exterior. When designing screens, consider the material of the screen, the size of the wire and the mesh, and the method of attachment to the building. The least expensive material is galvanized wire, but it is inadvisable for use in churches due to the high maintenance required to prevent rusting. Copper or bronze may also be used to fabricate screens, but they cost more than galvanized. If left unpainted, copper can stain the building, particularly light-colored stones. Stainless steel has the greatest longevity combined with the least maintenance, but is also the most expensive. Whichever material is used, it should be painted, patinated, stained, or otherwise darkened. The screens will then visually disappear to enhance the appearance of the stained glass and building from the exterior.

All stained-glass windows and their frames need routine maintenance to ensure a long service life. The PG should be designed to allow for periodic maintenance to the frames. Applied frames used to support the PG should cover as little of the original frame as possible. It is a misconception that covering the entire existing frame with PG will obviate the need for routine maintenance. The effects of ultraviolet radiation, heat, and moisture are rarely negated by PG, and are often worsened. When installed incorrectly, "protective" glazing becomes "destructive" glazing.

Most windows in the U.S. do not have to be protected from anything other than vandalism. The most stable, albeit most expensive, protective glazing system is an isothermal one. Screens, or laminated glass vented externally, provide excellent cost-effective protection against vandals when such protection is truly necessary. Aesthetically, all leaded glass looks best uncovered as originally designed; the challenge to the architect, client, or contractor is to devise other ways to improve security and minimize vandalism around the property (fencing, landscaping, lighting, etc.). The goal of the Protective Glazing Study is to raise the standards for protective glazing when it must be installed. As in all endeavors, the careful consideration of all existing conditions and options will result in the most successful solution.

For Further Details

This article is based on a 1994-1996 protective glazing research project by Inspired Partnerships, based in Chicago, for The National Center for Preservation Technology and Training. It is the first study of its kind undertaken in the U.S. The entire "Protective Glazing Study" is available from: *The National Center for Preservation Technology & Training, P.O. Box 5682, Nachitoches, LA 71497 (318)-357-6410.* ■

Neal Vogel has worked extensively in stained-glass preservation while working for the New York Landmarks Conservancy and as the Director of Technical Services for Inspired Partnerships, in Chicago, for the past eight years. He has surveyed over 280 historic stained-glass installations, has consulted on dozens of stained-glass restoration projects, and has authored many technical articles on stained glass.

The scientific investigation of ancient glasses

R. H. BRILL

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The Corning Museum of Glass

The scientific investigation of ancient glasses

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Corning Museum of Glass, Corning, New York, U.S.A.

During the past fifteen years many advances have been made in the scientific investigation of ancient glasses and early glass technology. These have resulted from improvements in instrumentation and from the application of entirely new techniques. The object of this paper is to summarise the current state of research, that is, to discuss the tools now available for such studies and to give some idea of how they can be used and the sort of questions we can hope to answer.

This will not be a review paper of the type that is developed around an exhaustive bibliography. The author has elected instead to present one person's view as to where the mainstreams of this research seem to be carrying us. In an effort to make this paper more useful to all readers, an attempt has been made to illustrate all the techniques discussed with new experimental findings, and to indicate, albeit sketchily, just how these findings can be interpreted meaningfully for the curator or archaeologist. (Readers unfamiliar with the chemical aspects of glass are referred to two papers intended primarily for the non-scientist.[1, 2]) This is not to say, however, that the only point to scientific studies of early glasses is to provide a service to the archaeologist and curator. If such were the case, then the vast majority of the work done to date would have to be regarded as fruitless, because as yet only very few objects have ever actually been dated or given a sounder attribution on the basis of chemical studies. This research is an end in itself, for it reveals to us a great deal about the technological skills and levels of understanding of those whom the late Professor W. E. S. Turner has called 'our forefathers in glass'.[3]

CHEMICAL ANALYSIS

Two approaches

The most familiar kind of scientific research in ancien glass is chemical analysis and, as Caley[4] has pointe: out, the subject has quite a long history. Througnou this history the ultimate goal, which always seems t have been implied, is that one day the chemica analysis of a given specimen of glass will allow a attribution to be made of its provenience, or date c origin, or both. This hope still persists, but it remain to be seen just how specific such attributions can eve be. They may never be more than broad or indefinit generalisations or they may turn out to be highl specific and restricted to just a few factories or place:

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There are two basically different, although related, approaches to the chemical analysis of ancient glasses. The first is to analyse large numbers of well authenticated specimens of fragments and vessels encompassing a wide range of places and periods. The analyses must be accurate where necessary and comprehensive in terms of elements determined. They must include a sufficiently large number of specimens to allow statistically significant inferences to be drawn. It is only in this way that a useful catalogue of ancient compositions can be compiled. We already know that the differences to be anticipated are not in the gross composition, because for practical purposes virtually all ancient glasses are of the soda–lime–silica variety. (Soda (Na_2O) was the predominant alkali in glasses until the medieval period, when potash (K_2O) came into use.) The meaningful variability appears only to be in minor, or trace, or 'trace-trace' elements.

Undoubtedly, the major contribution to this catalogue of data has been the work of Sayre and Smith.[5, 7] Their findings have systematised our knowledge to the extent that their work could well serve as a model upon which other such studies in glass could build in the future. The key elements in their present categories are K_2O and MgO on the one hand, and Sb_2O_5 and MnO on the other, but Sayre's most recent findings indicate that the long hoped-for useful pattern of trace-element concentrations, for example the rare earths, may be emerging.[8]

Other studies of this type have been conducted by Turner, Geilmann, Besborodov and the author, among others. Many of these results were summarised by Caley,[4] and a check list of more current research appears annually in the *Journal of Glass Studies*.

A second approach is the intensive study of individual objects of special importance, or small groups of closely related objects. In this type of study, not only chemical analysis but many other sorts of scientific experiments may be made in an effort to assemble as much information as possible about the glasses involved. One of the first studies of this type was that of the Portland Vase by Turner.[9] Some more recent examples are those of the Lycurgus Cup[10, 12] along with a group of similar dichroic glasses, and a group of early Mesopotamian glasses from Hasanlu, Marlik, and Tell al-Rimah.[13, 14] The analyst is usually severely handicapped in these investigations by the small size of the samples that are available. These saturation studies go beyond the simply descriptive stage and include an elucidation of the technique of manufacture and, if called for, an explanation of the chemistry involved. They should also meet the final test of laboratory duplication of the particular phenomena of interest.

The inevitable result of these studies is an ever-increasing admiration for the glassmakers of early times. While everyone has long admired the manual dexterity and the skill and patience of these craftsmen, we are just beginning to realise that early experimentalists in glass also had an unexpected delicacy of control, if not a comprehension, of some of the complicated chemical factors involved in their processes.

Supporting analyses of suspected early raw materials are potentially very helpful in interpreting analyses of the glasses themselves, but the information presently available on such materials is relatively sparse.[15-18] The more one looks at the possibilities, the greater is the inclination to proceed with caution. There is a great danger of being misled by insufficient data or by samples which are not truly representative of the materials used in early times.

Some useful methods

It is axiomatic in most areas of chemical analysis that there is no one method that is the most suitable for solving all problems which may arise, because each analytical method has its own peculiar advantages and limitations. This is certainly true for glass analysis. Where very precise determinations of major or minor constituents are required, gravimetric, colorimetric, titration, or atomic absorption techniques might be preferred, but if one is interested in trace element concentrations, spectrographic analysis, even with its inherently lower precision, may be more suitable. X-ray fluorescence is useful where samples cannot be taken, but it is complicated by matrix effects and can cause pronounced discolorations in some glasses. Glasses containing manganese, for example, quickly become solarised by certain x-rays. The resulting purple colour can be bleached thermally, but apparently only by heating to approximately 250° C or above, and such treatment would be extremely hazardous to early glass objects.[19] Other special instruments, such as the electron microbeam probe and x-ray milliprobe have found special applications.[20, 21]

An extremely valuable addition to these more conventional methods is neutron activation analysis. This method can be used to analyse very small samples non-destructively, and offers a wide versatility in the elements which can be determined and the ranges of concentration with which it can deal.[22] However, the facilities required are by far the most elaborate of all methods, including even access to a nuclear reactor. Nonetheless, we can expect a growing use of this method in the years to come because of the greater resolution now available in new detector systems and because of the convenience that comes along with the computerisation of the analytical schemes.[8, 22]

Thus the method to be chosen by an analyst under given circumstances depends very much upon the type of information desired, the size of sample which can be

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taken and sacrificed, the accuracy required, convenience, expense, and availability of facilities. In the sections which follow we shall present applications of all of the above methods and describe the circumstances which led to their choice.

An analytical 'round-robin'

If the various analytical programmes referred to above are to be of maximum value, they should be conducted in such ways that their results can be compared to one another. For example, if an analyst wishes to interpret his own data in terms of the compositional categories established by Sayre's work,[5] then he must first have some assurance that the results of his own analyses are essentially the same as would have been obtained by Sayre and his co-workers, had they analysed the same glass. In a more general sense, we must have this same assurance whenever analyses of different glasses by different laboratories are to be compared. Without this assurance, one can never be certain if any observed differences truly reflect differences in the compositions of the glasses or are due simply to errors or to differences inherent in the analytical procedures of the laboratories involved.

It often comes as a surprise to archaeologists and curators to learn that different laboratories analysing exactly the same glass may turn up disparate results. The truth is that the chemical analysis of glasses is a difficult undertaking and still remains in some senses an art. The reliability of an analysis is very much dependent upon the skill and experience of the analyst. The picture is further complicated, in terms of ancient glasses, by the fact that the compositions are very complex and the presence of some elements interferes with the accurate determinations of others. In order to evaluate the extent of agreement to be expected among different laboratories analysing the same glass, an analytical 'round-robin' was initiated in 1962 at the Sixth International Congress on Glass, largely at the urging of Professor Turner. In the intervening years four reference glasses, having compositions resembling those of ancient glasses, have been prepared and distributed to 36 laboratories.[23, 24] Analyses of these glasses have been submitted by 16 laboratories and are being evaluated statistically; the remainder of the laboratories plan to use the glasses for calibration purposes.

The results of this study have been slow in emerging, primarily because of the complex compositions of the glasses that had to be used.* In addition, the full interpretation of the results is difficult, because so many different analytical methods were used. Each individual analyst will be guided by his own criteria, and each may tend to see the results a little differently. Consequently, no attempt is being made here to provide a comprehensive or conclusive evaluation of the round-robin results.

The analyses submitted vary considerably in the methods used, the number of elements determined, and in precision and/or accuracy. Among the techniques employed were the 'classical' wet methods (incorporating combinations of gravimetric, colorimetric, flame photometric, atomic absorption, polarographic, electrolytic, complexometric, and redox titration determinations), emission spectroscopy, x-ray fluorescence, and neutron activation.

It is quite clear (as we all anticipated) that there is variation in the results reported by different laboratories; indeed in some cases the variation is very wide. Almost every laboratory reported in one instance or other a result that would appear questionable if judged only by deviation from the results of the rest of the laboratories. Much of this variability is due to differences in methods employed, and probably in calibration of the methods.

It is also clear that a great deal of excellent analytical work has been done on these glasses, and they should serve well as a set of analysed reference glasses for future studies. While there is still considerable doubt as to the 'true' values which should be adopted for some of the elements in these glasses, in view of the wide variability of the reported results, it should nevertheless be possible to arrive at values for most of the elements which will be within limits of precision acceptable for routine analyses of ancient glasses. Two independent statistical evaluations of the results, which have been prepared and distributed to participants, should soon be available to other interested persons. For the first time we now have a set of reference glasses which approximate fairly well the compositions encountered in ancient glasses, and therefore it should be possible for different laboratories to correlate their earlier results to a certain extent and, more importantly, to calibrate future analyses in reference to one another.

A careful statistical study of these results, since they encompass such a wide range of analytical techniques, should also make it possible to recommend procedures to be used for the determination of at least the critical elements involved in ancient glass compositions. Such recommendations could only be made by people primarily concerned with glass analysis, and it is hoped that some of the members of Sub-Committee A VIII on Reference Glasses, will assist in this. It must be kept in mind, however, that improvements in chemical analytical techniques come very quickly, and even in the few years that have elapsed since these data were assembled, some laboratories may have revised their procedures.

* Many of these analyses were carried out by laboratories not primarily concerned with the analysis of ancient glasses, and therefore had to be assigned a low priority. The members of Committee B are grateful to several members of Committee A who have spent a great deal of time and effort on this work.

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Table 1. *Results of the analytical round-robin*

K_2O (wt. %) Glass A Laboratory	Method*	Result	K_2O (wt. %) Glass B Laboratory	Method*	Result	MgO (wt. %) Glass A Laboratory	Method*	Result	MgO (wt. %) Glass B Laboratory	Method*	Result
15	s	8·1 (r)	19	s	1·5 (r)	18	s	3·6 (r)	22	t	2·41 (r)
19	s	4·3 (r)	4	f/g	1·21	22	t	3·58 (r)	18	s	1·86 (r)
18	s	4·0 (r)	18	s	1·17	4	t/g	3·38 (r)	4	t/g	1·53
16	f	3·2 (r)	9	f	1·16	30	?	3·2 (r)	8	g	1·40
8	f	3·05	8	f	1·15	12	g	2·85	30	?	1·2
13	f	3·00	13	f	1·14	8	g	2·85	11	s	1·2 (r)
1	f	2·95	6	f	1·14	1	f	2·85	13	g	1·15
14	g	2·92	16	f	1·1	13	g	2·80	12	g	1·15
12	f	2·85	7	f	1·07	14	g	2·76	9	t	1·15
6	f	2·83	22	f	1·06	19	s	2·7 (r)	19	s	1·1 (r)
22	f	2·81	30	x	1·0	7	t	2·68	1	f	1·10
30	x	2·8	12	f	0·97	6	f	2·62	14	g	1·09
4	f/g	2·77	26	x	0·88	9	t	2·60	6	f	1·06
7	f	2·75	1	f	0·88	11	s	2·5 (r)	7	t	0·92
26	x	2·71	14	g	0·84	16	s	2·2 (r)	16	s	0·85 (r)
9	f	2·49 (r)									
Mean value		2·86			1·05			2·75			1·18
Theoretical composition		3·01			0·30			3·01			0·80

Sb_2O_3 (wt. %) Glass A Laboratory	Method*	Result	Sb_2O_3 (wt. %) Glass B Laboratory	Method*	Result	MnO (wt. %) Glass A Laboratory	Method*	Result	MnO (wt. %) Glass B Laboratory	Method*	Result
15	s	2·6 (r)	12	t	1·20 (r)	1	x	1·19	4	?	0·50 (r)
11	s	2·0	7	g	0·80	8	c	1·15	16	s	0·4
14	t	1·91	14	t	0·73	30	?	1·1	15	s	0·32
12	t	1·90	4	?	0·69	7	t	1·07	8	c	0·30
16	s	1·8	11	s	0·6	22	c	1·06	7	t	0·30
13	t	1·79	19	s	0·54	6	f/c	1·05	18	s	0·29
1	x	1·74	18	s	0·51	4	?	1·04	19	s	0·27
19	s	1·70	8	c	0·45	12	g	0·96	6	f/c	0·26
7	g	1·68	13	t	0·44	13	c	0·90	30	?	0·26
18	s	1·42	16	s	0·4	19	s	0·89	1	x	0·25
6	c	1·41	6	t/c	0·34	14	c	0·88	12	g	0·24
8	c	1·4	15	s	0·32	15	s	0·81	22	c	0·23
4	?	0·83 (r)	1	x	0·31	11	s	0·75	14	c	0·23
			30	s	0·3	18	s	0·73	13	c	0·20
						9	c	0·45 (r)	11	s	0·18
									9	c	0·12
Mean value		1·70			0·49			0·97			0·26
Theoretical composition		1·81			0·40			1·22			0·25

* s—spectrography c—colorimetry —flame photometry atomic absorption g—gravimetry t—titration x—x-ray fluorescence
(r) Rejected before calculation of mean

In order to illustrate the variability observed we have set out in Table 1 the round-robin results for potassium, magnesium, antimony, and manganese in two of the glasses. These elements are all known to be of special significance in the compositions of ancient glasses.

Three examples

Choche

As an example of analyses carried out for the general compilation of ancient compositions, Table 2 gives combined quantitative and spectrographic analyses of 13 specimens of glass excavated at Choche, a site located between Seleucia and Ctesiphon (Figure 1).[25] The specimens are representative of types of small vessels excavated in strata dating from about 250–400 A.D. All but one have a pale or full green colour and a characteristic enamel-like weathering.

The glasses are of the expected high potassium–high magnesium type, and have not been decolorised, since neither antimony nor manganese is present as an intentional additive. The compositions of the first 12 samples are all very uniform: only sample 1252 is different. On an *a priori* basis this was suspected, because it has a somewhat different appearance from the others. It is a fragment of a facet-cut vessel of 'colourless' glass, with a black, flaky weathering crust.

Figure 1. *Fragments of small objects from Choche. Reading from upper left: CMG 1243, 1244, 1245, and 1246*

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Table 2. *Spectrographic and quantitative analyses (wt. %) of some Mesopotamian glasses*

	*Twelve glasses: Choche 1240–51 Minimum**	*Maximum**	*Mean*	*One glass: Choche 1252*	*Four glasses: Tel umm Jirin 1260–4 (composite result)*
SiO_2 (by difference)			~64	~68	~65
Na_2O			~15·5	15·3	14·3
CaO			~8·5	10·3	8·39
K_2O			~3·5	0·69	2·12
MgO			~4·5	0·84	5·15
Al_2O_3	1–2 (1)	3–4 (2)	~3·0	2·84	2·42
Fe_2O_3	0·5 (2)	1·1 (1)	0·77	0·4	0·6
TiO_2	0·12 (1)	0·20 (5)	0·18	0·03	0·16
Sb_2O_3			<0·01	<0·01	<0·01
MnO			0·05	1·0	0·8
CuO		0·01 (1)	<0·01	<0·01	0·02
BaO		0·03 (1)	0·01	0·10	0·03
SrO	0·01 (3)	0·05 (1)	0·025	0·10	0·05
Li_2O			<0·001	<0·001	0·002
B_2O_3			0·02	0·03	0·03
ZrO_2	<0·01 (1)	0·08 (2)	0·043	<0·01	0·01

The following components either were not found or were present below the levels indicated:

<0·01: Co, Sn, Pb, V, Cr, Ni, Zn, As
<0·001: Ag, Rb, Bi
<1 P_2O_5

* The number of samples having a given value is given in parentheses

It is of the low potassium–low magnesium type and is decolorised with manganese. In addition, the levels of iron, titanium, barium, strontium, and zirconium also differ significantly from the other Choche glasses. It could well be an import from a more westerly source.

For comparison we have also listed analyses of four vessel fragments collected at Tel umm Jirin, a Sassanian glassmaking site about 25 miles from Choche which is believed to date to the fifth–sixth century. The fragments are all from the bases of small blown vessels and range from green to 'colourless'. The most striking difference between these glasses and those from Choche is that they all contain additive amounts of manganese, but there are other minor differences which are also believed to be significant.

Aphrodisias

Behind all analytical studies of ancient glasses lies the implicit hope that analyses will reveal chemical peculiarities which can serve to characterise the wares of some particular factory, region, or period. Presumably these could result from the use of local raw materials or refractories, or from the personal idiosyncrasies of the glassmakers. For the most part, however, compositions tend more to be uniform.

There is, however, one small group of objects whose compositions seem not only to characterise a specific factory or localised region, but which also seem to be linked reasonably to a local source of raw materials. The site is Aphrodisias in Turkey: the glass consists of two pieces of cullet and a few vessel fragments: the elements involved are boron, lithium, and strontium: the raw material might be alkali from nearby lakes.

Figure 2 shows one of the pieces of cullet, which measures about 12 cm in greatest dimension and shows some contours suggesting contact with a crucible or tank surface.[20] It is a well melted, aqua green glass with few bubbles or imperfections, but now beautifully iridescent. The excavator dates the glass between the fifth and seventh centuries A.D. Spectrographic and quantitative analyses of both cullet and vessel fragments from Aphrodisias are given in Table 3.

The fundamental composition of the glasses is much the same as that of most ancient glasses. They are soda–lime–silica glasses with the expected impurity levels of alumina, iron, and titania, and they fall into Sayre's high potassium–high magnesium category. Neither the pieces of cullet nor the vessel fragments contain antimony, and the manganese level is so low that it does not seem to have been an intentional additive. The most unusual characteristic of all these glasses is a relatively high boron content, close to 1·0% (as B_2O_3), about a hundredfold greater than is usually

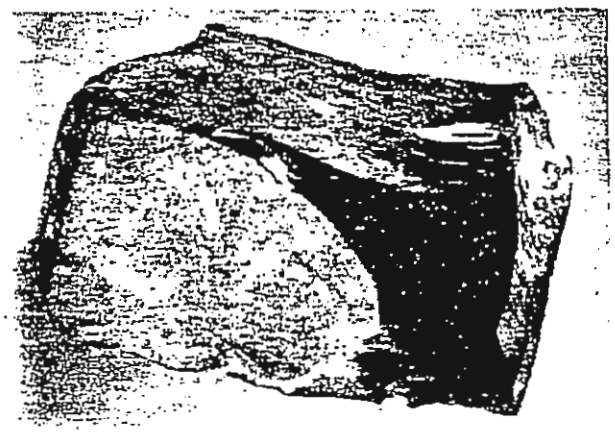

Figure 2. *Chunk of cullet from Aphrodisias which is unusual for its high B_2O_3 and Li_2O contents (CMG 590)*

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Table 3. *Analyses (wt. %) of glasses from Aphrodisias*

Description of samples

590, 591 *Two large chunks of cullet, about 12 and 20 cm in greatest dimension; aqua glass, few bubbles and imperfections, iridescent*
1110 *Fragment of solid lamp stem; green glass, slightly iridescent*
1111 *Fragment of stem of small footed vessel; aqua glass, slightly iridescent*
1112 *Fragment of base of vessel with radial raised decoration; greenish aqua glass, iridescent*
1113 *Fragment of solid lamp stem; dark green glass, little weathering.*
1114 *Fragment of small footed vessel; greenish aqua, iridescent*

All samples date from the fifth–seventh centuries A.D.

		Fragment number						
	*Method**	*590*	*591*	*1110*	*1111*	*1112*	*1113*	*1114*
SiO_2	d	~68	~68	~69	~70	~71	~67	~70
Na_2O	q	14·3	14·4	16·6	15·9	15·7	15·5	15·9
CaO	q	8·93	9·22	7·85	6·61	6·26	8·74	8·25
K_2O	q	1·20	1·27	1·64	1·42	1·43	1·73	1·47
MgO	q	4·18	3·60	1·57	2·29	2·45	3·43	0·58
Al_2O_3	q	1·70	1·64	~1·64	~1·64	~1·64	~1·64	~1·64
Fe_2O_3	s	0·6	0·5	~0·5	~0·5	~0·5	~0·5	~0·5
TiO_2	s	0·01–0·1	0·01–0·1	0·01–0·1	0·01–0·1	0·01–0·1	0·01–0·1	0·01–0·1
Sb_2O_3	s	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
MnO	s	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05
CuO	s	0·0001–0·005	0·0001–0·005	0·0001–0·005	0·0001–0·005	0·0001–0·005	0·0001–0·005	0·0001–0·005
SnO_2	s	0·01	<0·01	0·0005–0·005	0·0005–0·005	0·0005–0·005	0·0005–0·005	0·0005–0·005
PbO	s	0·01	<0·01	0·0005–0·005	0·001–0·01	0·001–0·01	0·0005–0·005	0·0005–0·005
BaO	s	0·01	<0·01	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05
SrO	q	0·11	0·11	0·22	0·17	0·16	0·19	0·17
Li_2O	q	0·14	0·15	0·15	0·14	0·14	0·14	0·14
Rb_2O	s	0·001–0·01	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
B_2O_3	q	0·90	0·87	0·94	0·94	0·91	0·98	0·98
V_2O_5	s	0·0005–0·005	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
Cr_2O_3	s	0·01–0·1	<0·01	0·01–0·1	0·01–0·1	0·01–0·1	0·05–0·5	0·05–0·5
NiO	s	0·005–0·05	<0·01	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05	0·005–0·05
ZrO_2	s	0·001–0·01	<0·01	0·001–0·01	0·001–0·01	0·001–0·01	0·001–0·01	0·001–0·01

Elements sought but not detected: Co, Ag, Zn, Bi

* d Estimated by difference
q Quantitative chemical analyses by flame photometry, complexometric and acidimetric titrations
s Spectrographic determination; composite of independent results from two laboratories

encountered.* In addition, the lithium content (as Li_2O) is also correspondingly higher, reaching a level in excess of 0·1%. Very often both of these elements are barely detectable spectrographically in ancient glasses. The strontium content (as SrO) is also rather high, but not uniquely so.

It seems very likely that the high B_2O_3, Li_2O, and to a lesser extent SrO, contents are a characteristic of one glass factory (or group of factories) supplying glass to Aphrodisias. The fact that the cullet was found on the site suggests that glass objects were made there. Furthermore, there is reasonable geological evidence that the cullet itself was made nearby, for there are lakes in Western Turkey, not far from Aphrodisias, where large deposits of colemanite are collected today. This colemanite, a calcium borate ($2CaO.\ 3B_2O_3.\ 5H_2O$), occurs in association with waxy, high lithium clays and the mineral celestite ($SrSO_4$).[28] If salts evaporated from the lakes in this region, or ashes from shrubs growing there, were used by the glassmakers as their source of alkali, the glasses might well be expected to contain high contamination levels of boron, lithium, and strontium.

Jelemie

There is another problem, often overlooked, which has a bearing on the interpretation of analytical data. The assumption has usually been made that the compositional variability within the output of a given factory will ordinarily be less than the variability among different factories. Indeed there are good reasons for making this assumption, but nevertheless no estimates have yet been made of the within-factory variability. The University of Missouri and the Corning Museum of Glass are co-operating to analyse some 60 samples of various types of vessels and cullet excavated at the fourth-century A.D. glass factory at Jelemie in Galilee.[29, 30] Excavation data indicate that the factory was probably in operation for not much more than 30 years (*c.* 352–383 A.D.). When these analyses are completed, we should have a good picture of the variability in composition of the output of one ancient factory over this interval of time. While the results will not necessarily be applicable to other situations they should be a useful index of what to expect elsewhere.

* Sayre shares this opinion (by private communication). Only four glasses among those that he has analysed show nearly as much B_2O_3 (0·3–1%). We ourselves have seen a tendency for glasses from Hasanlu, dating from *c.* 1000–850 B.C., to contain somewhat more B_2O_3 than other early glasses. Interestingly, all four of Sayre's examples are dark blue glasses coloured by CoO. We have also noticed that analyses by Farnsworth & Ritchie of XVIIIth dynasty glasses show that the B_2O_3 content of glasses from El Amarna is different from that of glasses from Thebes. Thus, two questions arise. Could there be a significant correlation between B_2O_3 and CoO contents in some glasses? Can Amarnan and Theban glasses be distinguished on the basis of their B_2O_3 contents? See Farnsworth & Ritchie[31] and also Tables LX–LXIII of Caley.[32]

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Neutron activation analysis

To the advantages of neutron activation analysis mentioned earlier may be added its capability of yielding accurate analyses for elements which are present in very low concentrations, even when only small samples are available. Several samples of special interest, including some diatretum fragments and dichroic glasses, are being studied now by Perlman and Asaro in co-operation with the author. We are reporting here some partial results because they follow up analyses presented at the previous International Congress on Glass, and illustrate the value of this method of analysis.

Three examples of dichroic glasses related to the Lycurgus Cup have been analysed and the results for gold and silver are set out in Table 4. Spectrographic analyses for similar examples are also shown, but only the sample from Sardis has been analysed by both methods. At first glance the analyses do not appear to agree very well, but when one recalls the extremely small samples available and the very low concentrations present, the semi-quantitative spectrographic analyses hold up rather well. The activation analyses are considered more reliable. It is apparent that the compositions of the Termancia Cup (Figure 6) and the diatretum fragment from the British Museum are both of the same species as the other dichroic glasses as far as the source of their dichroic colour effects is concerned.[12]

X-RAY FLUORESCENCE

Surface analysis

It is sometimes possible to turn the apparent disadvantages of an analytical method to one's favour. One of the principal shortcomings of x-ray fluorescence is that it yields only an analysis of the surface of the sample, which may not necessarily be representative of the material as a whole. But there are situations where the analyst may specifically want only a surface analysis.

Figure 3. *Fragments of Islamic lustre glass. Above, amber-stained, greenish transparent glasses; below, dark blue transparent glass with dense yellow opaque stain and olive transparent glass with bright red opaque stain*

Islamic lustre glasses

A notable example of this was a recent study of Islamic lustre glass (Figure 3),[32] in which the main objective was to determine the nature of the colourful decorative stains which extend down into the glass to a depth of about 20 μm. All the samples came from Fustat, and with the possible exception of the yellow- and red-stained glasses, were probably made there. The amber-stained glasses date from the tenth–eleventh centuries, but the yellow- and red-stained fragments are somewhat earlier, dating probably from the ninth or very early tenth centuries. X-ray fluorescence was an ideal means for obtaining comparative analyses of adjacent stained and unstained regions and, when combined with the results of several other types of experiments, these analyses were used to establish the basic chemical and physical character of the stained glasses and shed

Table 4. *Neutron-activation and spectrographic*[10-12] *analyses of some ancient dichroic glasses*

Sample	*Gold (p.p.m.)* *Neutron activation*	*Spectrography*	*Silver (wt. %)* *Neutron activation*	*Spectrography*
Termancia Cup, Roman, Museu Arqueologico Nacional de Madrid (21529)	12·6	—	0·098	—
Roman diatretum, British Museum (1953.10–22)	13	—	0·227	[illegible]
Cut Bowl, Late Roman, Sardis (G 63.18)	49·4	20	0·080	0·06
Lycurgus Cup, British Museum (1958.12-2.1) Fourth–early fifth century	—	40	—	0·03
Cut glass from Behnesa, possibly 4th Roman, Victoria and Albert Museum (691–1905)	[illegible]10	—	—	[illegible]

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Table 5. *Analyses by x-ray emission and emission spectrography of elements in stains of Islamic lustre glasses which are not present in the base glasses*

Colour of stain	*Number of samples*	*Elements Major*	*Minor—trace*	*Components found by x-ray diffraction*
Amber transparent	11	Ag, Cu	*Sn, Pb, As, Bi, Au; Hg (?)	Ag^0
Yellow opaque	6	Ag, Cu	Sn, Pb, S, Ni	Cu_2O, Cu^0 (trace), (Ag^0)†
Red opaque	3	Ag, Cu	Sn, Pb, Au, Bi; Sb (?)	Cu^0, (Ag^0)†

Elements sought but not detected: Zn, Sb

* Sn found in all stains; other elements in 1–5 stains
† Occasional traces, possibly from the superimposed silver stain

considerable light on the technology by which they were created. The experimental findings are summarised in Table 5. Interpretation of these findings involved their comparison with early Arabic texts, attempts to duplicate the stains by laboratory experiments, and the placing of the lustre techniques within the overall history of glass technology. The most significant conclusions, other than the purely chemical aspects, lay in the connecting role that lustre techniques played in linking together the earlier use of silver and gold in late Roman dichroic glasses with the later use of silver for the silver-stained cathedral windows of western Europe; and the possible links between the red opaque copper stains and the ruby glasses of stained glass windows.

The portable x-ray fluorescence spectrometer

This new instrument[21, 33] may prove to have several useful applications in the study of early glasses, as well as other archaeological materials. It can be taken to excavation sites and on field surveys, or into museums or other places where it can be used to analyse objects which cannot be removed or from which samples cannot be taken. A small radioactive source is used to excite secondary x-rays from the object to be analysed, and these are detected by a small probe connected by cable to the other parts of the apparatus.

The importance of this instrument lies not so much in the kind of analysis that it can do, because it does have some of the same limitations as all x-ray fluorescence analysers, but rather in the way in which it does the analysis. It should become very valuable for analysing large collections of sherds, for example, in museum storerooms in countries or institutions which do not permit the export or removal of samples for analysis. Trial experiments on weathered *opus sectile* inlays from Kenchreai and on stained glass fragments have proved the value of this method of investigation. These analyses were carried out by Perlman and Giauque in co-operation with the author.

The method is non-destructive, but in actual practice if the glasses are covered with an accretion of dirt, it is necessary to clean a small spot, perhaps 1 cm in diameter. One should also avoid weathered areas as much as possible. Because of the much lower dosage of radiation, there is no danger of discoloration as there is with conventional instruments.

The analysis of glasses from Kenchreai

Those familiar with the panels excavated by Scranton and his colleagues at Kenchreai,[34, 35] will recall that many of the glass inlays forming the designs, are very heavily weathered from centuries of submersion in the sea. Thus, for the most part, the glass inlays have lost their original colours, and the only direct way to tell what the colours were is to remove the weathering products from the inlays to examine the undecomposed glass in the interiors, if any remains (Figure 4). The author has found that chemical analyses of the weathering products are sufficient to allow one to identify indirectly the original colours of most of the glasses. But even so, it is obviously impossible to remove samples from the most important panels, such as the very striking one depicting Homer. Therefore, qualitative analyses for certain specific elements in the weathered inlays by means of this instrument could serve to identify the original colours of the glasses, and allow one to prepare accurate colour reconstructions of the panels.

The analysis of stained glasses

This instrument may also lead to an entirely new approach to the analysis of stained glass windows.

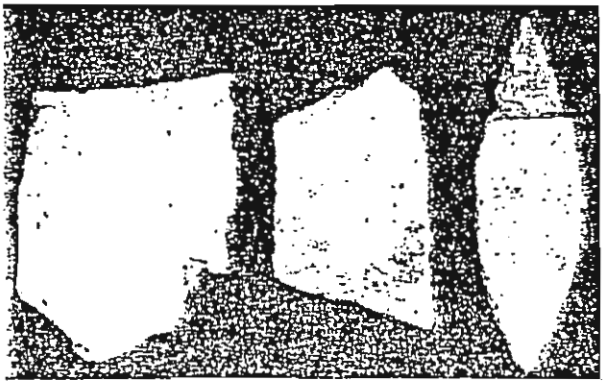

Figure 4. *Glass inlays from Kenchreai panels. Weathering products have been scraped away to reveal original yellow opaque colour*

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Previously it has always been necessary to work with excavated fragments, or samples removed from the windows or found lying loose in old workshops,[16, 17, 36] but it now seems quite feasible to obtain completely non-destructive analyses of representative glasses *in situ*. Such analyses might also provide a means for distinguishing replacement glasses in cases where visual examination is inconclusive, and analyses of the painted decorations could also be made at the same time.

Table 6 presents some results obtained with a portable analyser on 33 samples of stained glass of various colours from several geographical locations and of different dates. The sampling leaves something to be desired, but we were limited in this preliminary study to the samples most readily available. Even in these limited data, though, some encouraging signs can be seen. One would expect that, for the most part, the same elements would be present at about the same concentration in glasses of the same date in the same cathedral, and this has been borne out by the analyses (samples 58 and 59). There are also indications that the elements present in glasses from different cathedrals do indeed differ significantly from one another (samples 541, 60, 69, 71, and 79). Some glasses from the same cathedral but of different dates also differ significantly (samples 69 and 70 compared with samples 65, 66, 67, and 68). There is even one case where the ruby glasses from two nearby cathedrals of similar dates resemble one another more closely than the glasses of other colours within their own cathedrals, as if they might have been made in the same workshop from special cullet or ingredients. (See for example the Rb_2O contents of samples 72, 74, and 75. These three samples, along with 67, contain significantly more PbO and have the lowest MnO contents of the glasses analysed, reinforcing still further their similarities.) All of the ruby glasses were found to be copper rubies, with apparent CuO contents ranging from about 0·1 up to 1·6%. There do not seem to be any particular correlations with concentrations of other elements, except that most of the rubies contain SnO_2; several glasses of other colours, however, also contain SnO_2. Surprisingly, ZnO was found in 26 of the 33 glasses,

Table 6. *Analyses of some early stained glasses by portable x-ray fluorescence spectrometer*

	Provenience	*Date*	*Colour*	*MnO*	*Fe_2O_3*	*CuO*	*ZnO*	*Rb_2O*	*SrO*	*ZrO_2*	*Ag_2O*	*SnO_2*	*BaO*	*PbO*
51	Canterbury	1200–25	Green	2·1	1·1	0·05	0·1	0·02	0·05	0·02	—	0·02	0·10	0·2
52	Canterbury	1200–25	Ruby	0·9	0·6	0·4	0·7	0·02	0·03	0·02	—	0·02	0·07	0·2
53	Canterbury	1200–25	Amber	1·4	0·5	—	0·05	0·04	0·07	—	—	—	0·20	0·1
54	Canterbury	Late fifteenth century	Pale green	1·2	0·7	—	0·05	0.02	0·05	0·01	—	—	0·10	0·1
55	Coventry	Thirteenth–fourteenth century	Green	0·9	0·8	0·1	0·05	0·03	0·04	0·02	—	0·01	0·14	0·1
56	Coventry	Thirteenth–fourteenth century	Ruby	1·3	0·5	0·3	—	0·03	0·06	—	—	0·05	0·14	0·3
57	Coventry	Thirteenth–fourteenth century	Amber	1·2	0·5	—	—	0·03	0·06	0·01	—	—	0·24	0·1
58	Winchester	c. 1400	Colourless	1·2	0·8	—	0·05	0·03	0·06	0·02	—	0·02	0·13	0·2
59	Winchester	c. 1400	Green, silver-stained	1·2	0·6	—	0·05	0·03	0·06	0·02	0·02	0·03	0·14	0·2
60	Norwich	1400–50	Colourless	1·5	0·5	—	0·05	0·02	0·07	0·03	—	—	0·33	0·2
61	Batalha	Fifteenth or sixteenth century	Pale green	1·0	0·7	—	0·05	0·02	0·05	0·01	—	—	0·21	0·1
62	Batalha	Sixteenth century	Green, silver-stained	0·5	0·4	—	0·1	0·02	0·05	0·02	—	—	0·11	0·1
63	Batalha	Fifteenth century	Ruby	0·9	0·5	0·2	—	0·02	0·09	0·02	—	—	0·18	0·2
64	Batalha	Sixteenth century	Ruby	0·9	1·0	0·1	0·05	0·01	0·05	0·01	—	—	0·20	0·2
65	Nürnberg, St. Sebalds	1379–86	Pale green	1·5	1·5	0·1	0·1	0·05	0·07	0·01	—	0·01	0·21	0·5
66	Nürnberg, St. Sebalds	1379–86	Pale blue	1·7	0·9	0·15	0·2	0·04	0·06	0·01	—	—	0·24	0·2
67	Nürnberg, St. Sebalds	1379–86	Ruby	2·0	0·5	0·15	0·1	0·04	0·05	—	—	0·02	0·19	0·5
68	Nürnberg, St. Sebalds	1379–86	Amber	0·8	0·2	0·05	0·05	0·04	0·06	—	—	—	0·15	0·2
69	Nürnberg, St. Sebalds	1480	Amber	0·8	2·3	—	0·1	0·03	0·15	0·03	—	—	0·4	0·4
70	Nürnberg, St. Sebalds	Seventeenth century	Colourless, silver-stained	0·8	0·4	—	—	0·02	0·07	0·02	0·12	0·02	0·19	0·1
71	Nürnberg, St. Lorenz	1600–1700	Colourless	2·4	0·4	—	0·05	0·02	0·13	0·03	—	—	0·30	0·03
72	Nürnberg, St. Lorenz	c. 1476	Ruby	0·6	0·4	0·7	—	*	0·07	*	—	0·01	0·19	1·0
73	Ulm	c. 1400	Dark blue	0·8	0·6	0·15	0·05	0·03	0·06	0·01	—	—	0·21	0·3
74	Ulm	c. 1400	Ruby	0·4	0·3	1·6	—	*	0·07	*	—	0·03	0·18	2·0
75	Ulm, Chor-Fenster	1410	Ruby	0·7	0·5	0·7	0·1	*	0·07	*	—	0·03	0·18	3·0
76	Ulm, Chor-Fenster	1410	Yellow-amber	1·0	0·3	—	0·05	0·05	0·06	0·01	—	—	0·21	0·2
77	Speyer Dom	c. 1170	Ruby	1·3	0·4	0·3	—	0·03	0·05	0·01	—	—	0·18	0·1
78	Speyer Dom	c. 1170	Yellow-amber	1·1	0·7	—	0·05	0·02	0·05	0·02	—	—	0·28	0·1
79	Oppenheim	c. 1300	Pale green	0·8	0·8	—	0·05	0·02	0·10	0·02	—	—	0·24	0·2
526	Chartres	c. 1225	Pale blue	0·9	0·6	0·1	0·05	0·02	0·04	0·01	—	0·02	0·12	0·1
527	Chartres	c. 1225	Amber	0·8	0·5	0·05	0·05	0·02	0·14	0·02	—	—	0·10	0·1
528	Chartres	c. 1225	Ruby	1·0	0·5	0·8	0·1	0·02	0·04	0·01	—	0·02	0·13	0·1
541	Zerek Camii	Twelfth century	Mulberry	4·3	2·3	0·1	0·15	0·01	0·07	0·01	—	0·01	0·04	0·2

* No analysis due to interference of PbO

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with the ruby sample from Canterbury containing about 0·7%. Only the silver stained glasses showed the presence of silver. Manganese, as might be expected was found in all of the glasses.[16]

As with all methods of analysis one must be careful to determine just what it is that has been analysed. For example, some of the ruby-stained glasses analysed in this study consist of ruby flashings on a 'colourless' glass, while others consist of thin layers of ruby glass laminated within a 'colourless' glass matrix. Since the x-ray fluorescence technique yields essentially a surface analysis, the results on two differently structured glasses may not be strictly comparable.

Of course many more analyses are required before the particular inferences mentioned above could be proven, or compositional patterns discerned, but the point of these experiments was to make a quick survey of stained glass fragments to see what the possibilities are for further research. Even the scant evidence presented here seems strong enough to justify some complete analyses of a few stained glass cathedral windows *in situ*. We hope it will be possible to initiate experiments of this sort in the near future.

THE ELECTRON MICROBEAM PROBE

Opacifiers in inlays from the Kenchreai panels

The electron microbeam probe, although not suitable for the routine analysis of ancient glasses, has been used very effectively for special applications such as the non-destructive analysis of miniature mosaic plaques and millefiori glass, and also for the analysis of microscopic inclusions.[37, 38] The first application is especially valuable, for there is really no other means by which these objects can be analysed, for to remove a sample, even one small enough for spectrographic analysis, would be to destroy a significant part of the object. Even if one were willing to do that, it would be impossible to take a sample from all the glass components of these miniature designs without cross contamination.

Among the inclusions analysed were flakes of opacifiers, devitrification stones, incompletely fused batch stones, metallic inclusions, and weathering products. These results have been presented in detail elsewhere so they will not be discussed here, but there is one recent application which should be mentioned, because it employed a technique not available when the early work was done. These experiments consisted of recording the characteristic x-ray emission images which conform to the spatial distributions of selected chemical elements in samples of some ancient yellow opaque glasses.

As will be discussed below, Rooksby, in his studies of yellow opaque glasses, has shown that a changeover occurred from the use of an early lead–antimony pigment ($Pb_2Sb_2O_7$) to a lead–tin pigment ($PbSnO_3$) about, or prior to, the fourth century A.D. Therefore, while investigating the glasses from the panels found at Kenchreai, which date from approximately the period of this changeover, it was surprising to find that some of the yellow opaque glasses contained both tin and antimony, as well as lead. X-ray diffraction did not show conclusively which of the yellow pigments was present in the glass, or whether both were present.

An electron microbeam probe analysis was carried out on a flake of yellow opacifier measuring about 230 μm in its greatest dimension. From the coincidence of the distributions of lead and tin in this flake, shown in Figure 5, it is apparent that it is undoubtedly a flake of $PbSnO_3$, that is, the later form of the pigment. (Some lead is also dissolved in the glass itself.) On the other hand, similar images proved that the antimony occurs separately from the tin and lead. The antimony-rich regions, which are few in number, contain no lead, indicating that the antimony which is present is not in the form of the $Pb_2Sb_2O_7$ pigment. An image for calcium indicated that there is an excess concentration of that element (above the background of that found in the glass) which coincides precisely with the antimony-rich zones. This implies that the antimony is present in the form of $Ca_2Sb_2O_7$, a form of white

(a) Lead (b) Tin

Figure 5. *Characteristic x-ray fluorescence image showing distribution of lead and tin in a flake of yellow opacifier in glass inlay from Kenchreai panel (CMG 980). The congruence of these two images indicates that the opacifier phase is the lead–tin oxide pigment, $PbSnO_3$. Field measures about 0·20 × 0·25 mm*

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Figure 6. *Photograph and cross-sectional diagram of fragment of the Termancia Cup. The thickness is approximately 2·5 mm*

opacifier in use at the same time as the early form of the yellow pigment, $Pb_2Sb_2O_7$.

Probably this glass had been made by melting together two or more glasses which originally contained the late $PbSnO_3$ yellow pigment and the early $Ca_2Sb_2O_7$ white pigment. This has a definite bearing on the understanding of the nature of the Kenchreai glasses, as discussed in a later section.

MICROSCOPIC EXAMINATION

Of all the scientific means used for the study of early glasses there is none as versatile and valuable as low power microscopic examination. In a way this is ironic, because this use of the microscope is not primarily as a scientific tool. It is instead an extension of the experienced eye, and as such, it is a tool that can be used by the curator or private collector just as effectively as by the chemist or physicist. A microscope with a zoom lens is suitable and, although maximum magnification need not exceed 30–60×, stereoscopic viewing is crucial for visualising contours and spatial relationships. Provisions should be made for viewing with both transmitted and incident illumination.

Microscopic examination is extremely useful for the authentication of objects,[39] particularly for verifying whether a glass is ancient or new, for the detection of skillfully done restoration and repair, and for deciding whether an object is really made of glass or of some other material. This last question arises more often than one might at first expect, and the number of instances where clear-cut decisions are difficult become more numerous as one becomes less inclined to be guided by first reactions.

Microscopic examination is also helpful for learning more about how objects were made. For all the discussion that has taken place, we still do not have, or in some cases have not had until recently, a complete understanding about just how some of our most important types of early glass objects were made. Prime examples are cored vessels, diatreta, fused mosaic plaques, gold glass, and early ribbed and hemispherical bowls. We shall certainly learn more about the cored vessel techniques from papers at this Congress,[40, 41] one of which describes the use of a sophisticated type of microscopy, petrographic examination, involving the preparation of thin sections of a variety of cored vessels.

Some diatretum fragments

As an illustration of how microscopic examination can be used, Figure 6 shows a photograph of a tiny fragment of the Termancia Cup[12, 31] together with a sketch of another similar fragment examined by the author. The striations which stand out prominently in the photograph are undoubtedly due to slight inhomogeneities in the oxidising-reducing character of the glass introduced during gathering. These subsequently led to the uneven precipitation of colloidal metal resulting in the banded appearance. As shown in the sketch, the 'grain' of the glass in the posts is parallel to that in the wall section or, to put it another way, the posts have been carved against the 'grain' of the glass, suggesting strongly that this section (and presumably the rest of the vessel) was cut from a single thick-walled blank. Unfortunately, the one fragment examined does not contain much of the post section, and therefore it is not possible to state this conclusion definitely. However, examination of other more suitable post and cage fragments should serve to settle whether or not this was the case.

Similar evidence was observed during the microscopic examination of fragments of two other diatreta, one from Conimbriga which has been dated as fourth–fifth century A.D.[42] In both of these pieces, although only very limited specimens were available for examination, small elliptical bubbles were observed in post fragments. In every case (about seven bubbles altogether) these were slightly elongated perpendicular

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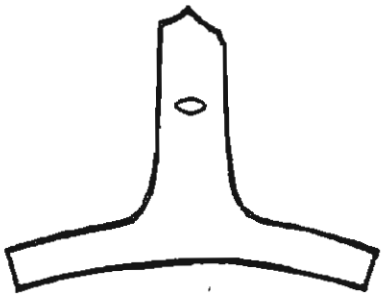

Figure 7. *Drawing of the cross-section of a fragment from a diatretum found in Conimbriga showing an elongated bubble in the post*

to the direction of the post, that is to say, parallel to the plane of the wall surface (Figure 7). Also, no discontinuity planes could be found near the regions where the posts joined the walls. This is very strong evidence that these parts of these two vessels were also cut from single thick-walled blanks. Similar conclusions were drawn concerning a diatretum fragment from Corinth.[43]

In other cases, of course, the evidence may not always be so obvious, but striations, bubbles, and discontinuities can all provide very substantial evidence, which when carefully thought out can lead one to equally conclusive findings. A word of caution must be added, however, because microscopic observations, just like all others, can be misleading if one does not interpret the observations against suitable examples of comparative materials. The greatest danger is in confusing an observation which is consistent with a given hypothesis for an observation which enables one to reject alternative hypotheses. In fact, it is almost a general rule in archaeometric investigations that it is easier to disprove an idea than to prove one.

X-RAY DIFFRACTION

A useful adjunct to chemical analysis is x-ray diffraction, a means for identifying the crystal phases present in a material. It has found several valuable applications in the study of ancient glasses, including the identification of colorant-opacifiers and imperfections such as devitrification stones and partially reacted materials. X-ray diffraction requires only very small samples and is therefore an especially useful tool for the analyst of ancient materials.

The identification of opacifiers

The most important x-ray diffraction studies of early glasses were carried out by Rooksby, his earliest work having been done in collaboration with Turner.[44–48] Studies of opacifiers have also been made by Werner & Bimson.[49–50] Rooksby and Turner studied the opacifiers in a selection of over 70 glasses, covering some 3500 years of glass history. One of their most significant findings is that the white and yellow colorant–opacifiers used during the first 17 centuries or so of glassmaking, were always the calcium–antimony oxide, $Ca_2Sb_2O_7$, for white glasses, and its companion lead–antimony oxide, $Pb_2Sb_2O_7$, for yellow glasses. Rooksby's observation of the changeover from $Ca_2Sb_2O_7$ to SnO_2 (tin oxide) and the coincident changeover from $Pb_2Sb_2O_7$ to '$PbSnO_3$', which seems to have taken place by the middle of the fourth century, probably marks a pivotal point in glass technology. Noting that both involve the substitution of another element, tin, for antimony it seems likely that this could be related to the changeover, noted by Sayre, from antimony to manganese as a decoloriser, which apparently began during the first century and had been completed by the fourth century A.D.[6]

A very interesting x-ray diffraction study of some Chinese opaque glasses by Werner & Bimson[49] showed that fluoride opals were being used in China as early as the Tzang period (A.D. 618–707). This use of fluoride, in the form of CaF_2, preceded its use in the west by many centuries.

In Table 7 are listed a few selected yellow and white opacifiers identified in the course of other studies during the past few years. These examples will help to illustrate some of the ways in which x-ray diffraction information is useful in glass studies.

These results tend to expand Rooksby's generalisations geographically, although they do so in an entirely expected manner. The yellow and white opacifiers found in some early glasses from al-Rimah, Nuzi, Hasanlu, Marlik, and Nimrud are all the same lead and calcium antimonates he has identified, as were those found in early examples of mosaic tesserae, inlays, and other glasses from various sites. On the other hand, the lead–tin colorant-opacifier was found be be present in some of the later mosaic tesserae.

Of special importance are two yellow–green opaque tesserae, samples 488 and Pb-445. The first came from a second–third century A.D. mosaic from Antioch-on-Orontes and the second from a third-century mosaic at Seleucia Pieria, the port city of Antioch. Along with a yellow bead of the first century A.D. described by Werner & Bimson,[50] these samples show that the $PbSnO_3$ pigment was actually in use, at least in some places, prior to the fourth century. Sample 1119 is of considerable interest. The colour of the yellow opaque threading on this snake thread vessel from Caerleon is actually a little closer to the lemon yellow of the $PbSnO_3$ pigment than to the richer orangy yellow of $Pb_2Sb_2O_7$, but x-ray diffraction showed clearly that the colorant was the earlier $Pb_2Sb_2O_7$ pigment.

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Table 7. *Colorant-opacifiers in some ancient glasses*

Sample number	*Description*	*Colour**	*Phases present*
Pb-409	Tell al-Rimah, c. 1500 B.C.: threading from cored vessel fragment, glass completely weathered. (TR 3623)	(Yellow)	$Pb_2Sb_2O_7$
Pb-410	Tell al-Rimah, c. 1500 B.C.: cane from fused mosaic vessel, glass completely weathered. (TR 65-24-44, 49)	(Green)	$Pb_2Sb_2O_7$
1206	Nuzi, c. 1450–1350 B.C.: threading from cored vessel. (M100/1)	Yellow	$Pb_2Sb_2O_7$
1208	Nuzi, c. 1450–1350 B.C.: glaze from faience plaque. (G52: 30-2-170D)	Yellow	$Pb_2Sb_2O_7$
713	Hasanlu, 1000–850 B.C.: segmented 'frit' bead of quartz and yellow pigment. (HAS S-170)	Yellow	$Pb_2Sb_2O_7$
731	Hasanlu, 1000–850 B.C.: small yellow glass bead. (HAS S-103)	Yellow	$Pb_2Sb_2O_7$
Pb-429	Nimrud, seventh century B.C.: yellow glass inlay from ivory plaque. (ND 10,240)	Yellow	$Pb_2Sb_2O_7$
Pb-420	Rhodes, probably third–second century B.C.: lumps of yellow cullet from bead factory debris	Yellow	$Pb_2Sb_2O_7$
Pb-421	Rhodes, probably third–second century B.C.: lumps of yellow cullet from bead factory debris	Yellow	$Pb_2Sb_2O_7$
1119	Caerleon, A.D. 140–260 context; threading from snake-thread vessel. (54.389A, 491)	Yellow	$Pb_2Sb_2O_7$
276	Sardis, third–fourth century A.D.; mosaic tessera	Yellow	$Pb_2Sb_2O_7$
977, 978, 979, 980	Kenchreai, second–fourth century A.D. (?): glass inlays from *opus sectile* panels	Yellow	$PbSnO_3$
Pb-204	Shavei Zion, fourth–fifth century A.D.; mosaic tessera	Green	$PbSnO_3$
—	Shavei Zion, fourth–fifth century A.D.; mosaic tessera	Yellow	$PbSnO_3$
488	Antioch-on-Orontes, second–third century A.D.; mosaic tessera	Yellow-green	$PbSnO_3$
Pb-445	Seleucia Pieria, third century A.D.; tessera from the Mosaic of the Drinking Contest	Yellow-green	$PbSnO_3$
Pb-417	Denderah, Roman period; glass inlay	Red	Cu_2O
Pb-418	Denderah, Roman period; glass inlay	Orange	Cu_2O (trace $Pb_2Sb_2O_7$?)
1022 1024	Islamic lustre glass fragments, ninth to early tenth century A.D.; dense yellow opaque stains on dark blue transparent glass	Yellow	Cu_2O (trace Cu^{II} and Ag^{II})
715	Tell al-Rimah, c. 1500 B.C.: fused mosaic glass vessel. (65-24-49)	(White?)	$Ca_2Sb_2O_7$
701	Marlik Tepe, 1200–1000 B.C.; fused mosaic glass vessel	(White?)	$Ca_2Sb_2O_7$
711	Hasanlu, c. 850 B.C.: fused mosaic glass beaker. (HAS 64.130)	White	$Ca_2Sb_2O_7$
735	Hasanlu, c. 850 B.C.: fused mosaic glass beaker. (HAS 64.130, no. 4)	White	$Ca_2Sb_2O_7$
739	Hasanlu, c. 850 B.C.: fused mosaic glass beaker, weathered. (HAS 64.129, no. 2)	(White)	$Ca_2Sb_2O_7$
1121	Nimrud, seventh century B.C.: lump of blue opaque cullet	Blue	$Ca_2Sb_2O_7$
999	Cameo Cup, first–second century A.D.: white over blue. The Morgan Cup. (CMG 52.1.93)	White	$Ca_2Sb_2O_7$

* In parentheses when the original colour could not be determined visually

Analyses of a sufficient number of samples from the first to fourth centuries might some day define more precisely the apparent date or places of changeover from the antimony to tin form of the pigment. This of course could be of help in dating objects which are not precisely dated by other means, one example being the glasses from Kenchreai.

Among the coloured inlays incorporated in the Kenchreai panels,[34, 35] the yellow opaque glasses (Figure 4) are fairly well represented, and the white opaque less so. It will be recalled that the panels are not at present well-dated, but seem to date from somewhere between the second and fourth centuries A.D. Therefore, it was of considerable interest to know which forms of the opacifiers these glasses contained. Chemical analyses showed that tin is copiously present in many of the glasses, including the yellow opaques, but antimony is also sometimes present.

On the basis of the analyses one would guess that the white opaques were coloured by $Ca_2Sb_2O_7$ (since little tin is present) and that the yellow opaques were probably coloured by $PbSnO_3$, but the picture is confused by the sporadic presence of antimony (up to 1·2% Sb_2O_5) in the yellow glasses. X-ray diffraction showed that $PbSnO_3$ was definitely the primary crystalline phase in all of the yellow glasses analysed, but there is a possibility that some very slight traces of $Pb_2Sb_2O_7$ could also be present in some of the yellow glasses with the greatest Sb_2O_5 contents. Unfortunately, the x-ray data for the white opaque glasses, which contained very little opacifier, were inconclusive, but the likelihood is that the white phase is really $Ca_2Sb_2O_7$ and not SnO_2. The question that arises is how to reconcile the apparent contradiction in finding the early form of the white pigment with the later form of the yellow pigment. This led to the electron microbeam

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Figure 8. *Fragment of completely weathered cored vessel from Tell al Rimah: Greatest dimension 4·6 cm. Although the colour is no longer visible, x-ray diffraction showed the presence of $Pb_2Sb_2O_7$ (CMG Pb-409)*

probe analysis discussed earlier, which resolved the chemical questions and paved the way for an archaeological interpretation.

The sensitivity of x-ray diffraction for identifying these colorant–opacifiers is apparent in the results of some of the other samples reported in Table 7. Among these are several bits of glass which, like so many examples of early Mesopotamian glass, are completely weathered through. In each case it was possible to determine what the original colours of these glasses were. Figure 8 shows one of the fragments, a cored vessel from al-Rimah. This glass is believed by the excavators to date from about 1500 B.C. One very small fragment of this glass was dissected, and it was found that no undecomposed glass remained within the interior of the fragment, but microscopic examination revealed a few tiny specks of yellow material in what had originally been a threaded decoration. These were submitted, still mixed with some of the weathering products from the glass, to x-ray diffraction analysis and the results clearly showed the presence of the $Pb_2Sb_2O_7$ opacifier.

We have examined a few pieces of yellow and orange opaque glasses which yielded curious results. This is a class of ancient glass objects consisting of some early Egyptian amulets (ordinarily dated from the sixth to third centuries B.C.), orange glasses which appear in inlays in Ptolemaic times, and orange tesserae used in mosaics up through the Byzantine period. X-ray diffraction of a number of these glasses has shown that the sole colorant is cuprous oxide, Cu_2O. This is of interest because the familiar natural form of Cu_2O is cuprite which has a characteristic brilliant red colour, and it is also well known that Cu_2O, sometimes with metallic copper, was the colorant in ancient red opaque glasses. Surprisingly, however, there are even some densely coloured yellow opaque glasses in which Cu_2O appears to be primarily responsible for the colour; and x-ray diffraction shows that the yellow opaque stains studied in connection with the analyses of Islamic lustre glasses (Table 5) also contain only Cu_2O. We believe that this colour variation is a particle size effect, which is also suggested by the results of several experimental melts.[51] This question is discussed further in the section on the scanning electron microscope.

Other applications

As mentioned before, there are other applications of x-ray diffraction to the study of ancient glass besides the identification of colorant–opacifiers. Many specimens of waste and refractory materials from the Jelemie excavations[29, 30] have been studied by this means, and tell us something about the types of by-products that accompanied the early manufacture of glass. X-ray diffraction also proved to be very useful in the study of the Beth She'arim slab.[52, 53] Because this glass was so highly crystallised, it was possible to learn a great deal about the thermal history of the glass and the way in which it was made.

One of the problems which arise most commonly in museum laboratories is that of identifying materials from which certain objects are made and, as noted above, it is surprising how often the question is raised in connection with objects tentatively identified as being made of glass. In cases where microscopic examination has not sufficed to answer this question, x-ray diffraction has often been very useful.[39] We have encountered several objects catalogued in various places as glass which have indeed been proven to be faience or other materials. There are also cases where the compact, highly fired form of Egyptian blue ($CuO, CaO, 4SiO_2$) closely resembles dark blue glasses microscopically, but x-ray diffraction can be used to distinguish between the two.

THE SCANNING ELECTRON MICROSCOPE

The scanning electron microscope is a new instrument having a maximum resolution somewhere between that of the conventional electron microscope and ordinary light microscopes. Its principal advantages are convenience of operation, ease of specimen preparation, and a greater depth of field than one ordinarily obtains with the light or transmission electron microscope. It is especially useful for examining surface topography, and several applications have been made in glass research.[54]

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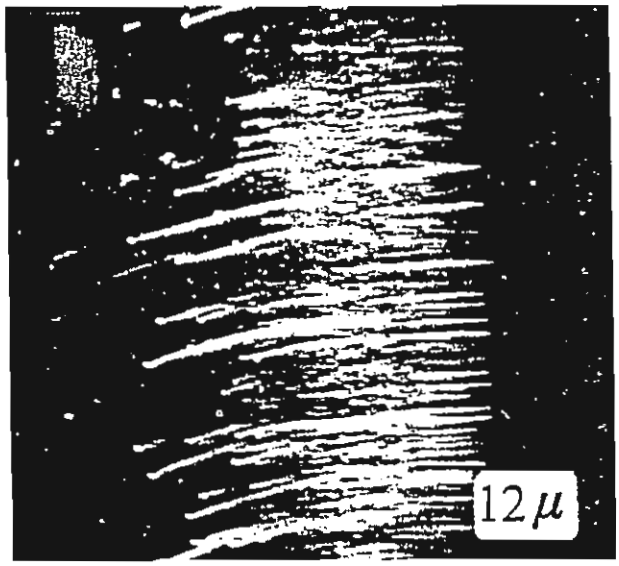

Figure 9. *Fractured cross-section of fragment of Islamic lustre glass. To the right is dense yellow opaque stained zone, and to the left in the unstained matrix glass. Curved lines are fractures originating from spheres believed to be cuprous oxide particles*

Figure 10. *Fractured cross-section of orange opaque glass from Denderah (Ph 418)*

Yellow stains and opacifiers

Some selected samples of ancient coloured opaque glasses and also some of the red- and yellow-stained Islamic lustre glasses discussed above have been examined. There are several questions related to the colours of these glasses, some of which bear as much on the fundamental physical chemistry of the glasses as on the historical aspects. We particularly hope that direct observations of the fine-grained particles of cuprous oxide (Cu_2O) in certain of these glasses will provide information on their sizes, shapes, and distributions, information which in turn may help in explaining the apparent dependency of colour upon particle size.

One of the specimens examined is a fragment of the dark blue transparent variety of lustre glass having a dense yellow stain, which extends some 20 μm into the glass (Figure 3). X-ray diffraction had shown cuprous oxide to be the only crystalline phase present in the stain, but microscopic examination up to a magnification of 400× was not capable of resolving the shape or showing the nature of the particles responsible for the colour. The scanning electron microscope revealed the presence of small spherical particles of the order of 0·5 μm in diameter (Figure 9). A micrograph of an orange opaque glass inlay from Denderah, also known to be coloured by cuprous oxide, shows a dispersion of similar particles which appear to be slightly larger (Figure 10). Thus, the difference in colour between the yellow and the orange glasses may be due to the difference in the sizes of these particles. For comparison, the micrograph in Figure 11 shows a considerably larger dendritic growth of cuprous oxide in a red opaque glass inlay also from Denderah.

ISOTOPE STUDIES

Isotope studies of ancient glasses, especially investigations of the isotopic abundances of lead and oxygen,

Figure 11. *Polished and etched cross-section of red opaque glass from Denderah (Ph 417) showing crystallisation of cuprous oxide in dendritic forms*

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have yielded important information. In the case of lead the information is related to the geographical origins of the ores from which the lead was smelted, while in the case of oxygen, the information concerns the nature of the raw materials.

The isotopes of most chemical elements are uniformly distributed in nature, that is to say, samples of the elements occurring in different places or different substances contain the same relative proportions of each of that element's isotopes. Where this is not so, the variations in isotopic compositions often provide valuable information. For example, the variation in the proportion of C^{14} to C^{12} is the basis of radiocarbon dating.

Lead

Lead is an outstanding exception among the elements. Because of the way they are formed, lead deposits of different geological ages can have distinctly different proportions of its four stable isotopes Pb^{204}, Pb^{206}, Pb^{207}, and Pb^{208}. Thus, lead ores coming from different geographical regions can often be distinguished from one another and many such determinations have been made over the years for geological purposes.[55] It has recently been shown that isotope ratios of lead which has been taken from ancient objects of lead or extracted from ancient materials containing lead can yield useful information about the mining regions from which the original lead ore could possibly have come.[56, 57]

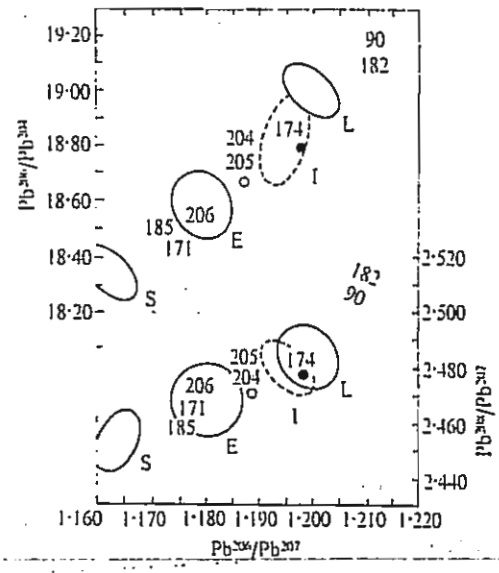

Figure 12. *Lead isotope ratios in archaeological objects. The enclosed areas represent types of lead often found. Numbers represent glasses from other sources cited in the original text*

- L Laurion-like lead
- E 'English' lead
- S Spanish, Welsh, and Sardinian lead
- I An empirical group containing some leads from Italy
- ● Lead from yellow opaque inlays from the Kenchreai panels
- ‥ Lead from red inlays from the Kenchreai panels

Figure 12 shows a somewhat oversimplified summary of the findings to date, which include determinations on some 120 samples of ores and lead from archaeological objects, including metallic lead, corrosion products, alloys, pigments, glazes, and glasses. The four letters S, E, I, and L indicate four of the types of lead which seem especially abundant in archaeological materials, but there are many samples in the gaps between them. There are several complicating factors in interpreting these data, and we refer the reader to the original publications for a thorough discussion of these factors, but we must indicate here two of them. First, leads coming from widely separated geographical regions may come from geologically similar deposits and, therefore, can be indistinguishable isotopically. Secondly, lead in early times, just as at present, was often melted down for re-use, and there was therefore a chance of leads from different sources becoming mixed together.

Recent work[51] has been principally concerned with the determination of isotope ratios of lead extracted from ancient glasses, such as the red and yellow opaques to which lead was added as an intentional ingredient. As yet only nine of these glasses have been studied, but the results of all are most interesting. There is nothing to be added at present to what has been said before about these samples, but there are two new samples which deserve some comment.

These samples were extracted from specimens of red and yellow opaque glass inlays from the Kenchreai panels. One of the questions connected with the panels is that of where they were made. Although they were found in Greece, it is very unlikely that the glass itself was made there since there is not thought to have been much glassmaking activity in Greece at that time. The panels depict Nilotic scenes, and their style strongly suggests Alexandria as the place of manufacture, but there is no tangible evidence which favours Alexandria rather than Italy, in the region of Rome or Naples, for example.

Before carrying out the experiments, it was realised that if a Laurion-like lead were found, this would not necessarily indicate that the glasses were made in Greece, because that type of lead has turned up in other places around the ancient world. On the other hand, any other result would rule out Greece as a place of manufacture, because Greece must still have been saturated with that type of lead, even though the Laurion mines are believed to have fallen into disuse some centuries before.

The results obtained for the two glasses were really

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quite unexpected, and although the discussion which follows may seem very involved, we include it here because the situation is quite typical of those that arise in the evaluation of experimental findings.

The most significant point is that the leads in the yellow and red glasses are distinctly different from one another, and must have come from different sources. This indicates either that the yellow glasses (or more specifically the yellow pigment) and the red glasses were made in different places, or that they were made in a place where different types of lead were in use, for example, a place where lead was not mined locally but was imported from different areas. It is possible too, that the inlays were fashioned from earlier glasses salvaged from different sources, as is also suggested by other evidence mentioned earlier in the present paper.

Unfortunately, it is difficult at present to relate these two leads to the groups shown in Figure 12, because the determinations were made at different laboratories using different techniques. Although the data are considerably more accurate than the earlier data in the Figure we do not know exactly how they are related. Thus, the final interpretation of the results will have to await the outcome of experiments which will allow us to redraw the boundaries of the groups. Nevertheless, we have plotted the points on Figure 12 to give the reader some idea of the logic behind the experiments.

The lead in the red glasses falls between Groups E and I, and may be the same as that found in two green and red tesserae from Shavei-Zion.[51, 57] The placing of the yellow glass is a little more ambiguous, because it falls near the boundaries of Groups L and I. In view of recent data, obtained on the same instrument with which these two glasses were studied, we are inclined to believe that the lead could be 'Italian' or, if it is like the Group L leads, that it resembles certain leads from Asia Minor more closely than the known Laurion leads. The lead in the yellow glass also resembles that in sample 174, a lump of red opaque glass found at Tara Hill in Ireland, but not believed to have been made there.*

None of this, however, alters the clear fact that the two leads are different from one another, and that at least one of them, that in the red glass, and possibly both, came from some source other than Laurion.

Oxygen

Oxygen isotope analysis may find even broader application. Whereas lead occurs in most early glasses only as a trace component, oxygen is universally present, accounting for about 45% of the weight of most glasses.

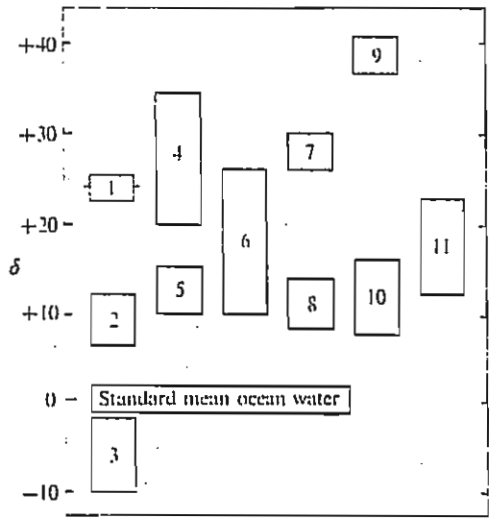

Figure 13. *O^{18} contents of some natural materials including a few used for glassmaking*

1. Atmospheric oxygen
2. Igneous rocks
3. Inland waters
4. Sedimentary quartz
5. Igneous and metastable quartz
6. Limestones
7. Shell hash
8. Some quartz sands
9. Natron
10. Various alkalis
11. Some early glasses

δ Deviation from standard in parts per thousand

The isotope of interest is O^{18}, which is not very abundant in nature, accounting for only one atom of oxygen out of about every 500. Since oxygen is relatively susceptible to fractionation, the O^{18} content of oxygen from different natural sources and from different types of minerals is quite variable. O^{18} contents are usually stated in terms of δ, the deviation from an accepted reference point on the scale of O^{18} contents of natural materials (Figure 13).[58-61] Realising that the various raw materials used for making glasses throughout history have come from sources which probably had differing O^{18} contents, it appeared worthwhile to investigate some early glasses to see if these differences might not be reflected in the glasses themselves.

The O^{18} contents of more than a hundred glasses have been determined by Clayton and Mayeda at the request of the author. They employed a technique perfected for the analysis of silicate rocks.[62] Although the work is still in progress and many questions remain to be answered, it already seems likely that these determinations may offer an entirely new means for characterising early glasses or, more specifically, for grouping glasses empirically, just as has been

* Since the preparation of this manuscript additional lead isotope determinations on about 50 ancient glasses and 90 ancient bronzes have been made by W. Shields, E. Catanzarro, and J. M. Wampler at the National Bureau of Standards. These data will prove very helpful in interpreting the results of glasses studied earlier, including those from Kenchreai.

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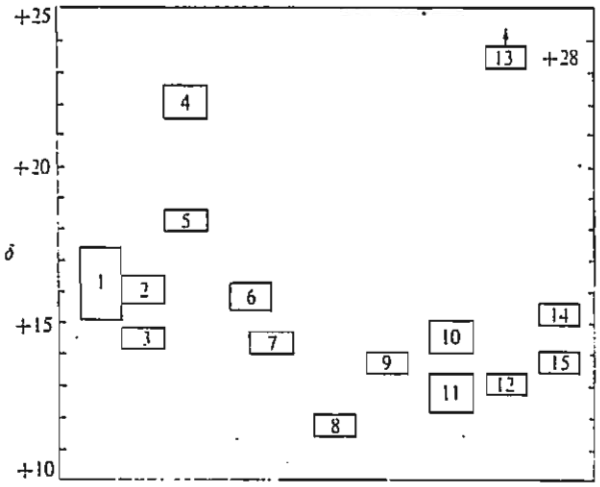

Figure 14. O^{18} *contents of some early glasses*

1. Six glasses of various colours: Egypt, XVIIIth Dynasty, c. 1350 B.C.
2. Two blue amulets: Mycenaean
3. Two blue glasses: Hasanlu, c. 850 B.C.
4. Four glasses, bowls, and inlays: Nimrud seventh century B.C.
5. One colourless glass: Persepolis, sixth century B.C.
6. Ten manganese-decolorised glasses: Rome and the Rhineland, first to fourth century A.D.
7. Five glasses, Jelemie, A.D. 352–383.
8. Three glasses: Islamic period
9. Three stained glasses: Chartres, c. 1225.
10. Four stained glasses: Nurnberg, St. Sebald, 1379–86
11. Three stained glasses: Speyer Dom, c. 1170
12. One bottle fragment: Port Royal, Jamaica, pre-1692
13. Weathering crust from sample 12
14. Two fragments of colourless glass: Amelung, c. 1790
15. Two fragments of green glass: Amelung, c. 1790

attempted by means of chemical analysis. Some typical values for the glasses are shown in Figure 14.

The first experiments with glasses melted under controlled laboratory conditions suggest that time and temperature of melting do not drastically affect δ of the resultant glasses, but that δ depends primarily upon the O^{18} contents of the original ingredients.

DATING METHODS

Perhaps no technique would be more welcomed by archaeologists studying glasses than a reliable and really workable scientific means for accurate dating. A number of techniques have been tried, but at present we certainly have no method that approaches general applicability. Among those that have been attempted, with varying degrees of success, are thermoluminescence dating, fission track dating, alpha particle recoil track dating, the isotope techniques of geochronology, and the counting of layers within decomposition crusts. Each of these techniques has shown either some utility or some promise for special cases, and they are frequently applicable to the ancillary materials excavated along with ancient glasses. They can sometimes provide means for showing whether given glass objects are ancient or modern, even though they do not provide precise dates.

Radiocarbon dating

The question is often raised as to whether or not radiocarbon dating can be applied to ancient glasses. The most straightforward answer is that it cannot, because the amount of carbon remaining in most glasses, usually in the form of dissolved carbon dioxide, is so small that a very great quantity of glass would have to be treated in order to extract a sufficient amount of carbon for a dating experiment. Moreover, the effective date obtained would not necessarily apply to the glass itself but rather to the raw materials containing carbon which were used in its manufacture. But the second qualification does lead one along another direction of thought.

Is it possible that the measurement of the apparent radiocarbon date of a piece of glass could be used to identify not the age of the glass but sources of raw materials? For example, given a sufficiently large quantity of glass which contains perhaps more carbon than is normally found, one could theoretically extract the carbon, obtain an apparent radiocarbon date, and then, if the actual date of the glass melting was known, gain some information on the various materials which introduced the carbon into the glass. One such extraordinary case has actually arisen, and although it is necessary to make many over-simplifying assumptions, we hope that we might collect some information pertinent to at least this one piece of glass. The glass involved is itself extraordinary. It is the huge slab of glass found in an ancient cistern at Beth She'arim, which was discussed in some detail at the last International Congress on Glass.[52, 53] In contrast to most pieces of ancient glass this glass loses about 3% of its weight upon heating at 1200°C. and a substantial part of this is due to the liberation of carbon dioxide dissolved in the glass.

By sacrificing about one pound of the glass and by careful melting *in vacuo* it was possible to collect about 0·17 g of carbon in the form of a barium carbonate precipitate. This was counted in a special low-level counting apparatus, but the results are not yet available. The author has also undertaken some supporting radiocarbon work on possible raw materials, such as ancient and modern natron and some beach sands.

Radiocarbon dates have also been attempted for some samples of plaster from the fourth century A.D. glass factory at Jelemie.[29] Although the results were somewhat sporadic it seems that more refined experiments should permit the dating of such plasters to become a more accurate tool.[63–65] The most serious

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complicating factor appears to be the incorporation of incompletely calcined limestone in the plaster.

Potassium/argon dating

The isotope techniques of geochronology, for example potassium/argon dating, do not at present appear to be sufficiently accurate to be used for dating man-made objects. Within the present limits of precision it would be possible to say that a piece of glass might be 2000 years old plus or minus 2000 years.

Thermoluminescence

This shows very great promise for the dating of pottery, but the results with ancient glasses at present do not look very encouraging. Natural thermoluminescence has been detected in a few samples, but not in others, and it is of interest that the more heavily devitrified glasses, for example, samples from the Beth She'arim slab, show a high natural thermoluminescence which might be associated with devitrification crystals. It is rather surprising that ancient glasses do not show thermoluminescence because, in a qualitative sense, virtually all glasses do fluoresce and one would imagine that a glassy network structure would be heavily populated with whatever traps are necessary for building up thermoluminescence centres. It may be that the transparency of the glass causes the centres to be bleached optically if excavated objects are exposed even momentarily to bright environments. In order to see if this was an important effect we have excavated in the dark several samples of glass at the site of Jelemie. These samples have been stored, cleaned, and prepared in only the subdued light of a red darkroom safelight. Unfortunately, the measurements on these samples have not yet been completed. The thermoluminescence of limestone materials associated with the walls at Jelemie and the tank at Beth She'arim has proved useful for showing qualitatively whether or not these have been heated, that is to say, whether or not they definitely were once parts of furnaces.

Alpha-particle recoil track dating

Initially this technique appeared to show promise for the dating of ancient glasses, since it does seem to apply to natural glasses and to minerals.[66] Unfortunately, two independent investigators[67, 68] both now doubt that the method will work with man-made glasses, but neither has yet entirely rejected the possibility that it can be of some use.

Fission-track dating

This method[69–71] has been shown to be useful for recent glass objects which contain of the order of 1% of uranium, but ancient glasses contain so little uranium that the amount of time required to build up an observable number of fission tracks in the glass is much longer than the ages of the glasses themselves. However, should ancient glasses be found which have a little more uranium in them it would, in principle, be possible to date them by this technique.

Weathering crusts

Another method that has been attempted for dating ancient glasses is the counting of the microscopically thin layers within weathering crusts.[72–78] Weathering is nearly universal among ancient glasses which have been exposed to sufficiently corrosive conditions. For the most part, because of the rather good corrosion resistance of most of these glasses, weathering shows up most often only as iridescence or thin weathering crusts, usually a fraction of a millimetre thick. But even in these cases the weathering crusts almost invariably have layered structures. (The only exceptions seem to be certain heavily leaded glasses.) There are occasional pieces which have particularly heavy weathering crusts which range from 1 mm up to about 4 mm in thickness and, when properly mounted and polished, it is sometimes possible to trace in them a continuous sequence of layers from the outermost surface in to the still undecomposed glass. If one accepts an annual (or nearly annual) rate of formation beginning at about the time of burial in the earth or submersion in water, then a count of the layers in the crust should correspond to the number of years elapsed since weathering commenced. The system is similar to that of dendrochronology, except that a deterioration process is involved rather than one of biological growth.

As a method of dating, this technique obviously can be applied to only a small fraction of the early glasses that have been excavated, if for no other reason than that so few pieces have sufficiently thick, intact weathering crusts. Moreover, the glasses with the least chemical durability, and therefore those most likely to be heavily weathered, are often also the least homogeneous and most poorly mixed. Therefore, they usually have irregularly formed, convoluted weathering structures, rather than the parallel, essentially planar layers seen in the more homogeneous glasses. Ancient beads are a notable example. Thus, when these glasses are examined, the weathering crusts must be visualised as three-dimensional structures, often interpenetrating one another, and must be treated accordingly. One must make special efforts to find a truly continuous path of layers, and not be misled into counting some layers twice or completely missing others.

The glasses most likely to be dateable by this means seem to be those ranging from the early eighteenth century back through the Medieval period. Roman

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and Byzantine glasses are generally too resistant to corrosion to become heavily weathered; Egyptian glasses are most often found in arid environments, and therefore have not suffered much from corrosion; Mesopotamian glasses are often so heavily weathered that no glass remains, and what does is too fragile to be handled.

Another interesting aspect of the phenomenon is the question of why the layered structures form. Two points are stressed here because they may not be evident to the casual observer. The layers in virtually every case are thin, physically separated, amorphous, siliceous layers, with closely conforming contours. The only exceptions recalled by this author are occasional pieces of glass from underwater sites, where the crust itself seems to be a physically intact body and the layers, though still apparent, seem to be more like discontinuities within that body. Also, the chemical mechanism proposed to account for the layer formation in terms of seasonal variations in temperature, or moisture, or both, has not been verified experimentally. It should be kept in mind, however, that any alternative chemical mechanism proposed to account for the layering must be relatively insensitive to temperature changes, otherwise the seasonal variations in temperature might lead anyway to an annual formation of layers. Thus the mechanism of layer formation still poses a most intriguing problem.

MUSEUM TOPICS

We had hoped to touch here upon two other aspects of early glass, but space will not permit it. The first of these was to have been a summary of the uses of a group of miscellaneous examination techniques including ultraviolet fluorescence, radiography, and polariscopic examinations, all of which should be applied as a matter of routine to important objects when they enter a collection. The second was to have dealt with the problems of storage and treatment of severely crizzled glasses. Although we cannot go into detail, we must call attention to the urgent need for further investigations of this latter topic.

If the problems of conservation are to be solved rationally and effectively, it is imperative that treatments and the specification of storage conditions be based upon an understanding of the chemical mechanisms involved in deterioration. Instances have recently been found where objects which once showed little or no visible crizzling have become noticeably more crizzled after having been installed in new exhibition surroundings. Apparently, after having become equilibrated with a moist, cool environment over decades (or even centuries) there are some glasses which undergo a form of deterioration which is not visible upon casual examination, and thus may go unrecognised. If such objects are later placed in dry, centrally heated buildings or exhibited in cases where they are warmed by intense illumination, the crizzling rapidly becomes more severe and glass can begin to spall from the surfaces. With so many museums modernising their installations and facilities, irreparable damage could be occurring now in many collections, without anyone realising what is happening. Therefore, we strongly urge curators to make periodic examinations of suspect pieces and to check through early photographic files to detect examples of this accelerated crizzling. We also call their attention to the recommendations on safe storage conditions for such objects.[79] Perhaps this whole area should be further investigated by Sub-Committee B III on Scientific Examination of Ancient Glasses with the advice and help of glass scientists from Sub-Committee A II on Durability.

Acknowledgements

It is difficult to acknowledge properly the assistance of all of the archaeologists and scientists who have contributed to the various research findings reported here. Because of the required publication format many acknowledgements which the author would have customarily included in the text proper have been placed instead in this appendix. We hope that the apparent formality of this means of acknowledgement will not detract from the genuine gratitude which the author now expresses to all those concerned.

Sources of samples mentioned in text and tables:

Glasses from Choche: Mariamaddalena Negro Ponzi, Istituto di Archeologia, Turin.

Glasses from Tell umm Jirin: the site was brought to the attention of the author by Robert McC. Adams, Oriental Institute, University of Chicago.

Glasses from Aphrodisias: Kenan Erim, New York University.

Sample of Termancia Cup: Luis Vazquez de Pargo, Museo Arquelógico Nacional, Madrid.

Sample of diatretum fragment: Anthony Werner, The British Museum.

Sample of dichroic cut fragment: Robert Charleston, The Victoria and Albert Museum.

Yellow opaque glass (1119): George Boon, National Museum of Wales.

Yellow opaque glasses (448, Pb-445): Richard Stillwell, Princeton University.

Yellow opaque glass from Tell al-Rimah: David and Joan Oates, British School of Archaeology in Iraq.

Diatretum fragment from Conimbriga: Jorge and Adília Alarcão, University of Coimbra.

Islamic lustre glasses: The Corning Museum of Glass.

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Stained glasses in Table 6: The Dean and Chapter of Canterbury Cathedral, Madeline Caviness, Dennis King, Brian Hobley of the Herbert Art Gallery and Museum, C. V. da Silva Barros of the Museu Nacional de Arte Antiga, Lisbon, Gottfried Frenzel, and A. H. S. Megaw.

Opaque glasses in Table 7: The British School of Archaeology in Iraq, The Semitic Museum, The University Museum (University of Pennsylvania), The National Museum of Wales, The Sardis Expedition, The American School of Classical Studies in Athens, The Department of Antiquities of Israel, Princeton University, and The Archaeological Museum, Tehran.

Glasses in Figure 14: To be cited in future publication.

Experimental work:

Spectrographic and quantitative analyses in Tables 2, 3, and 5, by C. A. Jedlicka and R. H. Bell of Lucius—Pitkin—Laboratories,—New—York—City; additional spectrographic and quantitative analyses in Table 3 by D. Kauser and B. van Voorhis of Corning Glass Works.

X-ray fluorescence analyses in Table 5 by D. Stephenson and D. Kimble of Corning Glass Works and C. A. Jedlicka.

Neutron-activation analyses in Table 4 by I. Perlman and F. Asaro of Lawrence Radiation Laboratory.

X-ray fluorescence analyses in Table 6 by I. Perlman and R. Giauque.

X-ray diffraction analyses in Table 7 by H. Holland, B. Gullo and J. Geiger of Corning Glass Works.

Electron microbeam probe analyses of Kenchreai glass by W. T. Kane and N. Binkowski of Corning Glass Works.

Scanning electron micrographs by E. Korda and R. Fritz of Corning Glass Works.

Thermoluminescence measurements by M. Han of University Museum, University of Pennsylvania and A. Liener of Bern University.

All experimental melts by A. A. Erickson of Corning Glass Works.

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THE USE OF EQUILIBRATED SILICA GEL FOR THE PROTECTION OF GLASS WITH INCIPIENT CRIZZLING

ROBERT H. BRILL

IN A PREVIOUS PUBLICATION[1] we have discussed glasses showing incipient crizzling, that is, glasses in the earliest stages of crizzling. This condition threatens many pieces of European, East Asiatic, and American glasses manufactured between the seventeenth and nineteenth centuries. Examples exist in public and private collections throughout the world. These glasses have absorbed moisture during their lifetimes, becoming hydrated to a depth of approximately 50 microns (0.05 mm). For some reason, however, possibly because they have been stored more-or-less continuously in moist environments, they have not developed the same severe surface crazing as that which characterizes the more familiar condition described simply as "crizzling." On glasses showing incipient crizzling, the damage may often be overlooked, for only when the objects are viewed in just the right light do the silvery, crazed patterns of early crizzling become evident. Nonetheless, these glasses are very unstable, and if exposed to low relative humidities for extended periods of time (ranging, perhaps, from several months to a few years) the glasses slowly release their water of hydration. This drying-out is accompanied by shrinkage in the affected layer which leads to the opening of fissures within that layer. The glass is thus transformed into a fully-crizzled state marked by a loss of transparency. If this degenerative process proceeds far enough, not only do the objects become unsightly, but a loss of surface material may also occur. The process is not unlike that which produces crackling when a layer of mud dries out in strong sunlight.

The chemical effects causing crizzling were discussed at length in the earlier publication, along with experiments in which the effects were reproduced in the laboratory. It was verified that the primary cause of crizzling is a deficiency in lime in the glass composition or an excess of alkali, two conditions which accelerate the hydration of glasses. Because it is believed that the degeneration of a glass with incipient crizzling into a severely crizzled state is the result of the loss of water of hydration, it seems reasonable to assume that in order to prevent degeneration, glasses with incipient crizzling should be stored or exhibited in relatively moist conditions, so as to inhibit loss of their water. With that aim in mind, storage at

1. Robert H. Brill, "Crizzling—A Problem in Glass Conservation," *Conservation in Archaeology and the Applied Arts*. London: The International Institute for Conservation of Historic and Artistic Works, 1975, pp. 112–134. The first stage of this research, that described in the above publication, was conducted in part under a grant from The National Endowment for the Arts.

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constant and moderate levels of temperature and RH was recommended. Moreover, it was recommended that dramatic spotlighting and regular cycling of temperature (as might be brought about by turning on and off gallery lights according to a daily schedule) both be avoided. It was concluded that ambient temperatures comfortable to people were fully satisfactory and that an RH of 45–47% should be the target, although any RH within a range of 40–55% would probably be quite safe. Short-term excursions to about 35% or 65% were thought to cause little harm, although long-term storage outside those limits might be harmful. From what has been learned in the meantime, these guidelines still seem valid.

It must be emphasized that by storing glasses under these conditions one can only hope to forestall the degeneration of incipient crizzling into severe crizzling. Storage under these, or under any other conditions which we can presently imagine, is not going to undo the damage already inflicted upon the glass, nor is it going to correct the inherent chemical instability and susceptibility to future degeneration.

It is the author's opinion that the same target conditions of temperature and RH are probably also as safe as any other conditions for the storage or exhibition of already-crizzled glasses. We see no advantage, and indeed see distinct disadvantages, to unnecessarily subjecting already-crizzled glasses to markedly more moist or markedly drier conditions than those specified for glasses showing incipient crizzling.

After the requirements for safe storage had been established, a schematic plan for an exhibition case intended to attain these conditions was prepared. The second stage of our work was to construct such a case and monitor its temperature and RH through a full year's cycle. That stage has now been completed, and the results are presented here.

The next stage of our work will be to design cases for glass installations in the new galleries of The Corning Museum of Glass which will open in 1980. It is hoped that the galleries themselves will be maintained between limits of about 35 and 65% RH as part of the architectural specifications, but there is no assurance that these will be met, and there are likely to be widely ranging short-term fluctuations. These conditions should probably suffice for the major parts of the glass collection which are not very susceptible to damage by RH changes. However, the crizzled glasses (especially those with incipient crizzling), certain glasses with painted or gilt decoration, and glasses with particularly fragile weathering crusts will require several individually controlled cases. Our present intention is that these cases will be controlled by equilibrated silica gel according to the guidelines listed below.

SUMMARY OF FINDINGS

The discussions which follow are likely to be of interest mostly to conservators and museum scientists. Therefore, so as to aid other readers, we present a summary of our findings here at the beginning of this article, along with some recommendations.

Although a great deal of useful information has been gathered, this stage of the project has been only partially successful.[2] We have demonstrated, to our own satisfaction, that storage in a case controlled by equilibrated silica gel is a valid, safe, and practical means for preventing glass with incipient crizzling from degenerating into a severely crizzled state. All the advantages anticipated for the system seem to have been realized. However, the experimental case used in the most important experiment, while it proved effective in isolating

2. We have certain reservations about publishing the results of only partially successful work, but the system seems as promising as ever, providing that proper corrections are applied, and the results complement nicely the findings of Thomson. Moreover, it will be another year before we can gather additional useful data, and we feel that others might benefit from knowing our experiences now.

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the glass from high exterior ambient humidities prevailing during the summer months, showed a persistent drift downward in relative humidity during the dry winter months. Because the dry winter months are the time when protection is most needed, questions arose about the usefulness of the system.

The main point of concern was whether the drift was the result of simple leakage—as was expected—or whether there was some fundamental flaw in the principle of the system. The appearance of two fine articles related to the use of conditioned (equilibrated) silica gel systems as this manuscript was in its late stages of preparation have pretty well settled our doubts. These two articles are by Nathan Stolow of the National Museum of Canada in Ottawa[3] and Garry Thomson of the National Gallery in London.[4] Both emphasize the problems of case leakage and provide guidelines for the quantities of gel required to compensate for leakage. It is apparent to us now not only that our case was not well enough sealed, but that the reservoir of silica gel was too small to prevent the downward drift under the extremely dry conditions prevailing in our galleries.[5]

Our findings and recommendations (stated in the form of intentions for our own new installations) are summarized as follows:

1. The equilibrated silica gel system is a valid, safe, and practical means for controlling RH in cases used for the storage of glass and is recommended for preventing the degeneration of incipient crizzling into full crizzling.

2. Leakage is a major problem. In all but the most extraordinary conservation systems, where the expenditure of extraordinary amounts of money and effort are warranted, it is wise to consider leakage inevitable. Instead of attempting to stop leakage altogether, it is probably much more practical to minimize it and compensate for the leakage that does occur. (One difficulty is the lack of any straightforward way of measuring leakage and therein lies part of the value of Thomson's theoretical treatment, which permits one to come to grips with the leakage problem.)

3. In our case designs for the Museum's new building, care must be taken to provide a sufficiently large quantity of equilibrating gel following the guidelines of Stolow and Thomson. The quantity of gel should be of the order of 20 kg per cubic meter of total case volume. (This is a four- to five-fold increase over what was used in our experimental case.)

4. It is probably more practical to use a few small exhibition cases than one large case. We will aim to have no controlled case larger than about 1.0–1.5 cubic meters in volume (including the equilibrating chamber).

5. The silica gel will be spread so as to present a large effective surface area to the air within the cases, and will be located, as much as possible, in close proximity to those objects it is intended to protect. Depending upon the nature of the individual cases, the gel will either be incorporated into fabric-covered panels or will be placed in open trays partially hidden by perforated surfaces. While we would like to minimize the presence of water-absorbent materials other than silica gel, on the basis that they introduce other variables into the system, those materials which are necessary will be selected with a view toward providing further beneficial buffering of the RH.

6. A separate conditioning apparatus will be constructed for the equilibration and reconditioning of the silica gel, and a back-up reserve of conditioned gel will be maintained.

7. A remote sensing RH and temperature probe system, similar to that described here,

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3. Nathan Stolow, "The Microclimate: A Localized Solution," *Museum News*, 56, No. 2, November/December, 1977, pp. 52–63. This publication also serves as an excellent entry into the bibliography on this general subject.

4. Garry Thomson, "Stabilization of RH in Exhibition Cases: Hygrometric Half-Time," *Studies in Conservation*, 22, No. 3, August, 1977, pp. 85–102.

5. As these words are being written, during the Great Blizzard of February 1978, the RH in our Museum's main gallery is about 12%.

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will be used to monitor case conditions and ambient conditions.

8. All lighting devices will be external and well-vented, with heat shields installed. No spotlighting will be used for dramatic effects unless it can be demonstrated that it produces no temperature increase in the objects.

9. We will consider the use of a "double-walled" barrier to attain longer hygrometric half-times. Thomson has shown that the hygrometric half-time depends upon the difference between the internal and average external RH. If an enclosed exhibition space is surrounded by another enclosed space containing silica gel equilibrated to the same target RH, then leakage from the inner chamber actually holding the glass objects should be much slower, because the gradient between that chamber and the surrounding chamber will be much smaller.

A few further remarks on the use of silica gel are worth repeating. Most readers already will be familiar with the use of silica gel as a desiccant, that is, as a material intended to absorb all the moisture from its surrounding air and leave the air as dry as possible. If the silica gel is itself dry to begin with, this is exactly how it behaves, because it has such a strong tendency to absorb water. In the present application, however, the silica gel used has already had water added to it in proportions of the order of 20–30 percent by weight. Hence, its tendency to absorb water has been much reduced. Silica gel containing this much water does not produce a near-zero RH in the surrounding air but instead, establishes an equilibrium RH of about 40–50 percent in the surrounding air. If the gel is the most abundant phase in a closed system and has a large surface area exposed, it will either remove moisture from the air or release moisture into the air until its own equilibrium RH has been established. Silica gel is well-suited for controlling exhibition cases because it is easy to handle, can be regenerated, does not become messy to handle in the hydrated state, and is chemically inert. In addition, its equilibrium RH, for a given water content, is said to be relatively insensitive to temperature changes.[6]

As with all conservation treatments or procedures, however, the silica gel system must be employed judiciously. In this instance, *judiciously* takes on a very important meaning because there is one way that the system could go seriously wrong.

As was described above, the whole efficacy of this system centers around one particular property of silica gel, namely, that it will release or take up moisture to maintain some constant RH in the surrounding air. This property of the gel is characterized quantitatively by its equilibrium Rh *vs.* moisture content curve, which describes what surrounding RH corresponds to what water content of the gel. During the course of this work, we have come to appreciate that this curve is not necessarily the same for all lots of silica gel. In fact, buying silica gel might be much like buying vegetables. A basket of corn bought in Petunia Pump last year might be quite different from a basket of corn bought in Pathan next spring, even though both are quite properly called "corn." So, for the present at least, we feel each new lot of silica gel should be regarded as a unique entity, and unless the manufacturer has provided an EMC *vs.* RH curve (an adsorption isotherm) the user must determine one himself.

Our recommendation to those who might consider making use of silica gel is, by all means, to go ahead but to be certain that the installation is supervised by a conservator or someone else who has a general understanding of how silica gel behaves. It is important first that care be taken to prepare the gel properly and to be certain that it is equilibrated to the target RH desired. (This process might take as long as a few weeks.) Then it is crucial that

6. Nathan Stolow, "Fundamental Case Design for Humidity Sensitive Museum Collections," *Museum News*, 44, No. 11, February, 1966, pp. 45–52.

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the RH of the system be reliably monitored. The danger is that if silica gel which is not sufficiently moist is used, or if the gel is allowed to dry out somehow, it could have the effect of drying out the glass and thereby cause harm. But this is not reason for alarm, for as long as the RH of the system is monitored, that should never happen. If the RH shows signs of drifting downward, the drift can be very simply corrected by adding water to the system; if it drifts upward, drier silica gel can be added. (In actual practice, this usually would be done by adding freshly-equilibrated silica gel.)

DESCRIPTION OF AN EXPERIMENTAL CASE

Because of budgetary limitations, we did not construct new cases for our experiments, but instead modified existing cases. At the outset it was realized that the results would not be ideal, and that the cases would not meet the optimum specifications. Nevertheless, the experiments served well to evaluate realistically a number of variables.

Our most important experiment made use of an aluminum-framed case with permanently-fixed glass walls on three sides and four large sliding glass doors on the front. The original top and bottom of the case were also of plate glass. The inside dimensions of the case are: height 1.66 m, width 2.87 m, and depth 40 cm. The volume of the exhibition case proper is approximately 1.900 l. It rests upon a steel base supported by six steel legs with a clearance of 45 cm beneath. The case contains three plate glass shelves mounted on adjustable steel racks.

The main advantage of this case for our experiment was that because it is made of plate glass and metal, it did not present surfaces which were highly absorbent to water vapor. The presence of fabrics or wood in a case is a complicating factor, as is demonstrated below in an experiment with a different case. The main disadvantage of the case was its sliding glass doors which were notoriously loose-fitting. The doors were sealed during the experiment with lengths of plastic tubing, used as gaskets, and duct tape. While this afforded a seal of sorts, it proved inconvenient to remove and replace the tape on those occasions when the case had to be opened. The interior seams of the case were caulked with a silicone caulking which worked fine, because it remained pliable and, therefore, would not have cracked if the case had shifted. (No build-up of fumes released from the caulking was detected.) Despite the effort taken, however, we know now that the case was not sealed nearly as well as we would have liked.

The original glass bottom was removed for the experiment, and a tightly-fitting, brazed sheet-metal compartment was fastened permanently in place beneath the case to serve as the chamber for the silica gel. Access to this lower chamber is through two gasketed, metal faceplates, held in place with sheet-metal screws. The exterior of the metal chamber was painted, but the interior surfaces were not.

The lower chamber contains six sheet-metal racks, each of which supports four enamel trays measuring 39.0 cm by 17.5 cm by 5.0 cm. The trays hold the equilibrated silica gel. In the experiment described, the silica gel filled the trays to a depth of approximately 1.5 cm. The exposed surface area, not corrected for granularity, was about 1.2 m^2. The trays were easily removed whenever necessary by sliding the racks out through the opened faceplates. The lower chamber is separated from the case itself by a polyethylene grid which provides adequate support for objects to be placed upon it while also permitting a free exchange of air between the lower chamber and the case proper. The volume of the equilibrating chamber is approximately 400 l, so that the total volume of the system (exhibition chamber plus equilibrating chamber) is approximately 2.300 l.

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During our experiments, it was found that no fan or circulating device was necessary, as there seemed to be sufficiently free exchange of air between the two compartments. This was helpful because it meant there was one less thing to go wrong and one less item in the system requiring maintenance. This case was not lit except by ambient room lighting, so no precautions were required against heat build-up from that source.

THE SILICA GEL

The silica gel used for our experiments had been prepared earlier by Dr. David Fischer, who worked at the Museum from January, 1973 to December, 1975 with the assistance of Mr. Joseph Maio, of the Museum's staff. In all, they equilibrated about 145 kg of silica gel. When purchased, the gel was nearly dry. Deionized, distilled water was sprayed directly onto the gel to hasten its absorption because storage with liquid water in a closed compartment proved to be too slow a means for equilibrating the gel. (Caution must be exercised when adding water to silica gel because heat is evolved by the process.) The amount of water added was calculated from data published by Stolow.[7] The curve reported in Dr. Stolow's publication gives relative humidity values for various equilibrium moisture contents of silica gel. (The equilibrium moisture content, or EMC, is the water content expressed as a percentage of the weight of the *dry* gel.) In Dr. Fischer's preparations, adjustments had to be made, which we assume resulted from differences between the silica gel we were using and that used by Dr. Stolow. The separate batches of moistened gel were then stored in double-thickness plastic bags inside galvanized metal cans which were then sealed with tape. Dr. Fischer measured equilibrium RH values for samples of the separate batches after the air above them in closed chambers had come to a constant RH. The results ranged from 43.5% to 47.8% RH. Measurements made two years later on the batch of gel actually used in our case experiment[8] agreed to within ±0.5% RH with Dr. Fischer's measurements.

Silica gel of 12–28 mesh was used. This was a compromise between two effects. The smaller the gel particles, the greater the exposed surface area and, consequently, the more rapid the equilibrium time. But it was thought that gel of too small a particle size might produce dust problems throughout the case. Actually, although we carried out tests specifically to detect dusting, none was found, and it was concluded that for the way we had introduced the gel (in horizontal trays), the 12–28 mesh size was fine. However, Dr. Stolow recommends using a larger size, 3–8 mesh, as mentioned below. (See A Final Note.)

A curve for equilibrium RH values *vs.* EMC for the gel used in this experiment was estimated by adding known weights of water to known weights of the gel, which had been dried previously at 190°C for seven hours. The water was added to the gel by evaporation transfer inside sealed 9.7-liter desiccator chambers. After the water had completely evaporated and the RH in the chambers had become constant—a process which required several weeks in some instances—the systems were assumed to have come to equilibrium. Samples of the gel were removed, and their water contents were determined by drying to constant weight at 180°C. The resulting EMC *vs.* RH curve is shown in Figure 1. Also plotted on this graph are data for three samples of silica gel removed from the Crizzling Case during an experiment described below.

The curve is displaced somewhat from the similar curve published by Stolow. Because we do not have a sufficient number of points for plotting both ascending and descending

7. Stolow, *loc. cit.*, p. 51. See also, A Final Note.

8. Davison, Code No. 408–08–72–201, Grade 408, Mesh 12–28, Package 9445.

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branches reliably, we have elected not to indicate hysteresis. Some of the points on the curve drawn were probably crossing over from the ascending branch toward the descending branch, and the three points for the samples withdrawn from the case should be on the descending branch.

The rather sharp bend in the curve near EMC -25% is of special interest. One wonders if such a plateau might result from saturation with water of hydration corresponding, for example, to $H_2SiO_3 \cdot H_2O$ ("EMC" -23%), $H_2Si_2O_5 \cdot 2H_2O$ ("EMC" -26%), or some other stoichiometric composition. Unfortunately, because of a very tight publication deadline, we have not yet been able to verify these data by repeat runs—and we confess to not having made a thorough literature search on the subject.

TEMPERATURE AND RELATIVE HUMIDITY MONITORING

The temperature and relative humidity of the sealed experimental case were measured by two sensing probes placed inside the case at diagonally-opposed corners. The probes were attached by cables to a humidity-temperature reader manufactured by the Phys-Chemical Research Corporation.[9] Although the system is designed to incorporate only one sensor probe, a special switch box was made which allows the system to accommodate twelve different sensors. These are attached by cables of various lengths (measuring up to 28 m) spread out in a network to various locations in the Museum where we chose to monitor the temperature and RH. The sensors were all individually calibrated by the manufacturer, and those used in the experiments described here were checked periodically against a sling psychrometer. The two probes in the experimental case check one another to within 2% of RH units.

It was decided not to record the data automatically, partly because it would have been very expensive, and partly because it would have been difficult to do that simultaneously for several sensors. In any event, there was no need for recording data automatically. For routine monitoring, four readings of temperature and RH were taken between 9 a.m. and 5 p.m. daily on each of the probes in the experimental case. During the hours when the Museum offices were closed, and on weekends, readings were taken by the Museum security guards on their rounds. Normally, four readings were taken each night. As each reading was taken, a notation was made of the weather conditions. When experiments had just been started or at particularly important stages, more frequent readings were taken. It is such an easy matter to collect data—one simply presses a button and reads the temperature and RH off two dials—that it is quite convenient to obtain nearly continuous data, providing only that one is willing to stay near the read-out meter for the interval required. The temperature and RH of the ambient air immediately outside the test case were recorded continuously on a recording hygrothermograph[10] which was in reasonably close calibration with the sensors, but which did not yield data of quite as high precision and accuracy.

In retrospect, the number of data taken during the course of the research described below—the Crizzling Case experiment, the monitoring of the Ravenscroft Case, the monitoring of three stations in the galleries, and the determination of the EMC *vs.* RH curve—is quite astounding. Some 20,000 individual readings of RH were recorded, along with an equal number of temperature measurements. This attests to the facility with which the readings

9. The instrument is a Humitemp-2 equipped with PCRC-11 HPT sensing probes. The address of the manufacturer is Phys-Chemical Research Corporation, 36 West 20th Street, New York, New York, 10011.

10. The instrument is a familiar one: model no. 5-594-2 manufactured by the Belfort Instrument Corporation of Baltimore, Maryland.

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are taken, for it never seemed at all a bother, and also emphasizes our indebtedness to the security guards who collected half of these data.

THE "CRIZZLING CASE" EXPERIMENT

The case described above was closed on August 25, 1976, after 12 kg of equilibrated silica gel had been spread out in the enameled trays. It was monitored according to the schedule outlined above (about nine readings per day) until September 20, 1976, when the relative humidity had leveled off at 44%. Then, 120 objects of glass, 15 with incipient crizzling and 105 already-crizzled pieces, were placed in the case, and it was resealed. The presence of the objects in the case appeared to cause the RH of the enclosed air to drift downward over the course of three weeks to a level of 40%. Evidently, the crizzled glass absorbed moisture from the air more quickly than the silica gel could replenish it. At that point, liquid water was added to the system in order to elevate the RH. This had to be done five more times over the succeeding year to keep the RH from dropping below the 40% level. In most instances, the water was sprayed directly onto the surface of the gel (see A Final Note, below), but occasionally it was added as liquid water in small beakers distributed throughout the case. This latter procedure is definitely not recommended (see A Special Precaution, below). Whenever water was added, the gel was always lightly raked to expose a fresh surface. Sometimes a slight crustiness was found to have developed on the surface of the gel after it had been in the case for several weeks. This was accompanied by a faint yellowish coloration.

From the above it is clear that the presence of this large number of crizzled objects with their large effective surface area altered the RH within the case, and that this effect is not negligible. This is to be expected, because where two absorbent phases are present within a closed system, the actual RH established should be intermediate between the individual equilibrium values for the two phases. If the equilibrium RH values of the two phases are very different, and if a much greater effective surface area of either phase is present, the net result would be that water would be "pumped" from one phase to the other, forcing the less abundant phase to absorb or desorb moisture until it could tolerate the equilibrium RH demanded by the more abundant phase. In this experiment the equilibrium RH values of the crizzled glass[11] and of the silica gel are quite close to begin with, and the effective surface areas seem well balanced against one another, so no extensive transfer of water from one phase to the other occurred.

The case was taken through more than a full year's cycle during which it became well stabilized for nearly six months from April until October at a level of 40–43% RH. During that interval, the ambient RH changed from 40% to 65% back to 40%. During the winter months, however, a gradual drift downward could be seen, and it was this which had to be compensated by the addition of liquid water to the system. From mid-October until mid-March, when the central heating was on, the RH just outside the case was rarely above 25% and frequently below 20%, sometimes remaining for more than a week at a time at 12–14%. We attribute the drying out of the case to exchange with this very dry air by leakage. The temperature and RH history of the experimental case is summarized and plotted in Figures, 2, 3, and 4.

Perhaps the most significant point is that the silica gel buffered the RH changes in precisely the way it was intended to do. Setting aside for the moment the drift caused by leakage, it is very satisfying to see that the short-term fluctuations are so small. It will be recalled that one of the advantages of using silica gel is

11. See Miscellaneous Notes.

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that its equilibrium RH values are said to have but a small temperature dependence, so that when the temperature changes, the gel still tries to maintain virtually the same RH. This was borne out in several instances where after abrupt temperature changes occurred, the RH was restored to its starting value, lagging behind by only a few tens of minutes.

During the course of these experiments, no visible changes occurred in the objects in the cases—but then none were anticipated. (See the exception in the note below.) The changes which would occur in crizzled glasses or glasses with incipient crizzling over a year would not be expected to be noticeable at the RH level maintained. That, after all, was the point of the experiment. However, changes on a microscopic scale should be monitored in future experiments. Some such experiments were underway at The Corning Museum of Glass in 1971, wherein tapes were applied to make microscopic replications of crizzled surfaces, and the tapes were recorded by electron microscopy. However, the original tapes were destroyed in the 1972 flood, and the work has not been revived, because there is a certain danger in such experiments. To put a tape on the surface of a crizzled glass is to risk the removal of any loosely-attached material on the surface, and we have been hesitant to run that risk.

THE "RAVENSCROFT CASE"

As part of a special exhibition mounted at the Museum in 1976, a fine example of English glass, a goblet made by George Ravenscroft in 1676, was exhibited (CMG no. 50.2.2). This vessel bears a raven's head seal, which Ravenscroft used to mark his later glasses made with a corrected formula. These glasses, he supposed, would not be susceptible to crizzling, as had some of his earlier glasses.[12] Nevertheless, Ravenscroft's corrected formula did not produce really stable glasses, and this particular object shows clear signs of incipient crizzling. It is a prime example of the sort of glass which must be carefully protected. If it is not, it will surely deteriorate into a severely-crizzled condition.

The object was to be exhibited in a small case constructed of plywood. The exhibition compartment volume was 68 l. The case was designed originally to be lit from above with spotlights, since it was to be located in a darkened gallery. The interior of the case was lined with about one square meter of purple felt, which complicated control of the relative humidity, as the felt tended to absorb a great deal of moisture. The case was made reasonably air-tight by sealing it with duct tape around all seams. A sheet-metal trough covered with the same felt and lined with polyethylene bags was placed in the rear of the exhibition compartment. Then 1,500 g of equilibrated silica gel was placed in it. A sensor was suspended unobtrusively in the rear of the case, and the case was carefully tested before the Ravenscroft goblet was installed. A mock-up of a colorless glass laboratory beaker was placed where the goblet was to be and lit with a twelve-volt lamp of a sort which frequently has been used throughout the Museum. The temperature readings as measured by a thermistor thermometer—which accurately measures the temperature of the glass, and not just the surrounding air—showed that illumination with this light raised the temperature of even this colorless glass from 27.0 to 37.5°C. This was judged to be completely unacceptable for illumination of the Ravenscroft glass in its unstable condition. When a plate of heat-absorbing glass and a piece of diffusing material were placed between the lamp and the exhibition chamber proper, the surface temperature of the glass dropped to 32.5°C, which was still

12. There are numerous accounts of Ravenscroft's early experimentation. One is: A. Hartshorne, *Antique Drinking Glasses*, New York: Brussel and Brussel, 1968, pp. 240–241.

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regarded as a bit high, and which was still warmer than the air in the chamber. The spotlight was replaced with a fluorescent lamp having external circuitry and the temperature then held at about 25°C, and did not differ measurably from the temperature of the surrounding air. Therefore, the modified lighting was deemed safe for the Ravenscroft object.

In an effort to make the exhibit more instructive, a volume from the rare book collection of the Museum Library was placed in the case with the goblet. This is a 1662 edition of Neri's *The Art of Glass* (Special Collection no. 327). The volume was opened to a page relevant to the chemistry of the Ravenscroft goblet. When placed in the case, the book produced a startling drop in RH. It absorbed water vapor rapidly, because it had been shelved under low-humidity conditions for several months prior to being incorporated in the exhibition. This is dramatic evidence that the presence of additional absorbent materials—in this case the felt and the book—has an important effect on the RH finally attained. Even as effective a controlling agent as the silica gel had a hard time coping with these complications. If one is attempting to control a case with a material like silica gel, we believe it is inadvisable to introduce any strongly absorbent materials unnecessarily. For our installation of the Ravenscroft object, water was added to the system in order to elevate the RH somewhat. After the addition of 65 g of water to the 1,500 g of gel, a safe and stable RH of 42–45% was established and maintained for twenty-four weeks, after which the exhibition was dismantled. The Ravenscroft object appears to have been completely unaffected by its exhibition experience.

THE HYGROMETRIC HALF-TIME

Garry Thomson's treatment of the stabilization of relative humidity in exhibition cases[13] makes use of the concept of a hygrometric half-time, that is, the time required for the RH of a case to drop halfway to the RH level of drier ambient air. His mathematical treatment assumes an exponential decay of the RH in the case and takes into account the rate of air leakage and characteristics of buffering materials within the case. We have tested Thomson's model by comparing it to the empirical data collected during the monitoring of our own Crizzling Case. Thomson's model predicts that a plot of ln(C-R) *vs.* t should yield a straight line. (C is the RH within the case at time t and R is the RH of the surrounding air.)

A plot of our data for the interval between December 12, 1977 until January 23, 1978 (Fig. 5) does indeed yield a straight line verifying that the decay is exponential. (R is known to have averaged about 22% during this period.) From the slope of this plot the decay constant, k, was found to be 0.0192 per day, and the calculated half-time is 36.1 days. From our EMC *vs.* RH curve an average value of M -5.9 was assumed, and in our experiment, B is known to have been -3.5 kg/m³. Therefore, by using Thomson's equation *vi*[14] and our own experimentally determined rate constant (k), it was possible to calculate that during that interval our case was undergoing about 2.3 air exchanges per day with the ambient air. This figure seems somewhat high and may not be real, because there could have been another factor contributing to the downward drift. Water had recently been added to the system and the silica gel might still have been in the process of reequilibrating. This would cause a downward drift if the rate of diffusion of water into the interior of the gel grains was relatively slow.

In our designs for cases for the new museum building, we will make use of Thomson's model

13. Thomson, *op. cit.*

14. Thomson, *ibid.*, p. 96.

$k_N = \frac{0.173}{MB \div 0.173}$ where M = moisture gain in g per kg for 1% RH rise and B = dry weight of buffer in kg/m³.

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and equation by increasing B, the quantity of buffering gel used, and attempt to reduce k by improving sealing so as to reduce leakage. In addition we shall explore still another approach.

Thomson's explanations make clear the fact that the leakage rate of the case is dependent upon the RH gradient between the case and its surroundings. His treatment quantifies the intuitive notion that the driving force behind leakage is the difference in RH and suggests that one way of extending the half-time of the drying process is to find some means to reduce the term (C-R). This, in turn, suggests that the presence of an air envelope of RH close to C surrounding the case would inhibit loss of moisture from the case and brings to mind the possibility of using a double barrier to further stabilize the case. This is just another way of looking at the rather obvious fact that a double-walled container would be slower to dry out but emphasizes that this would be especially true if the space in between also contained buffering material.

We have explored this possibility from a mathematical viewpoint and believe that a considerable extension of hygrometric half-time could be realized. The ultimate value of such a system would be determined by balancing the advantage of increasing the half-time against the inconvenience and expense of constructing a more elaborate case. Such a balance can be made favorable only by the ingenuity of the case designer.

SOME MISCELLANEOUS NOTES

"The Vapor Pressure" of a Crizzled Glass

A group of five badly-crizzled eighteenth-century French goblets was placed in a chamber with one of the same sensor probes used for monitoring the crizzling case. The chamber used was a 9.7-liter laboratory desiccator, although only the crizzled glass was placed in the chamber and no desiccant or other materials. When the experiment was started the relative humidity was 46%. The RH slowly drifted downward and after eight weeks, leveled off at 41%. If one disregards the effect of absorption and desorption of water vapor on the walls of the chamber itself, it might be inferred that the "vapor pressure" of the adsorbed water and water of hydration of this particular crizzled object is -7.2 mm Hg, or an RH of 41% at 20°C. This corresponds, within experimental error, to the value of 42% given as the equilibrium RH for the monohydrate of potassium carbonate cited by Robert Organ.[15] It also makes sense that the vapor pressure of water on—and/or in—a crizzled glass should be of the order of 40% or greater. Historically, the glass would have become hydrated to the extent that its equilibrium vapor pressure, expressed as an equilibrium RH, would be close to that of the average ambient RH it experienced over the past three centuries, and that value probably would have been of the order of 45%.

In a separate experiment, one of these goblets was heated at 110°C for one hour and its loss in weight, presumably consisting of evolved adsorbed water and water of hydration, amounted to 0.13 g or 0.12% of its weight.[16] The surface area of the goblet is about 278 cm^2, so its water content had been about 0.00047 g/cm^2. The same object was then saturated with water by letting it stand in a chamber at 100% RH for several days, and the heating repeated. This time the loss in weight amounted to 0.17 g or 0.16% of its weight, and a water content of about 0.00061 g/cm^2.

15. R. M. Organ, "The Safe Storage of Unstable Glass," *Museums Journal*, 56, February, 1957, pp. 265–272.

16. We thank Dr. Yao Su and Theresa Magliocca of Corning Glass Works for carrying out this determination.

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Reequilibration Times

For the system being tested to be used successfully, it is necessary not only that the silica gel release or absorb water as required, but also that it do so quickly enough so as to prevent the RH from wandering outside the safe levels specified. In order to evaluate the gel in this respect, a few simple experiments were conducted in laboratory desiccator chambers.

The capacity of the chambers used was 9.7 l. Approximately 90 g of silica gel removed from the enamel trays of the experimental case was placed in a covered glass dish inside the chamber. Then either a small quantity of freshly dried silica gel desiccant or a small quantity of liquid water was placed alongside the dish. The chamber was closed and allowed to dry out or build up a high RH. The chamber was then opened slightly and the dish of equilibrated silica gel was uncovered and the desiccant or any remaining water removed. Thus, the uncovered dish of gel was exposed suddenly to rather high or low RH conditions, and the time it required to restore the RH to its own equilibrium RH was recorded by a sensor probe enclosed in the chamber. In both cases the gel responded quickly.

In one experiment, the gel adjusted a starting RH of 69% to 41% in about two hours. In another experiment, it adjusted a starting RH of 13% to 40% in about four hours. It is probably true that a small-volume system reequilibrates more efficiently than a large system, but since the ratio of the chamber volume to exposed gel area was about the same in these experiments as it was in the large experimental case, it was surmised that the recovery time of the large case must be well within acceptable limits.

An experiment on the Crizzling Case itself showed that when the case was flushed out with ambient air at 17% RH, the silica gel reestablished its equilibrium RH of 40% within about eight hours. (The increase to 35% RH, 75 per cent of the way, required only two hours.)

A Special Precaution

Usually, when water had to be added to the system, this was done by removing the trays of silica gel and spraying or squirting a measured volume of distilled and deionized water onto them. On a few occasions, however, liquid water was added by placing it in twelve small beakers distributed throughout the case. In these instances, the RH rose temporarily, but not excessively, because the water evaporated more quickly than the gel could take it up. No harmful effects were noticed until the third time this was done. On that occasion, some water was sprayed onto the gel and some placed in the beakers. The moistened gel was evidently even slower in taking up water vapor from the air. The RH rose to a level of 70–80% and stayed in that range for about fifteen hours. At that time, it was noticed that one of the objects, a Venetian goblet (CMG no. 59.3.20), had become separated at an old repair and collapsed sideways. Fortunately, it did not fall, for if it had, it certainly would have broken badly, and could have taken other objects with it. Upon examining the rest of the objects in the case, it was found that two others had similarly become unglued. No real harm was done, because all of the separations were at old breaks. We mention this not only as a precaution against adding water to a system in this way, but even more importantly, as a warning that edge-to-edge joins made with epoxy resins, as these had been, can apparently be loosened by rather short-term exposures to an RH of the order of 70–80%. This was totally unexpected by us and should be noted very carefully by all those who handle repaired glasses.

Short-term Variations in Relative Humidity

Careful observations were made of small variations in RH which occurred over a matter of a few hours or a day. Normally, these variations

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were no greater than one or two percentage units of RH, but a few changes as great as three or four percentage units were observed. Generally these larger changes were accompanied by changes in temperature. When a temperature change of five or six degrees occurred, which occasionally happened, the RH would usually change correspondingly; that is, a rise in temperature would cause a decrease in RH until the silica gel could reequilibrate the system. But sometimes a rise in temperature was associated with a rise in RH, as if one were watching a classical adsorption experiment, in which the substrate releases the adsorbate as the temperature rises. These are small but interesting effects, and the processes should be studied further. In this connection, the fact that the RH of a given silica gel is thought to be relatively insensitive to temperature changes implies that the equilibrium partial pressure of water vapor over the gel must rise with temperature at about the same rate as the vapor pressure of water does.

Storage at Low Relative Humidity

In our earlier research several experiments were carried out on a Silesian goblet dated to 1820 which was donated for experimental purposes by Mr. Jerome Strauss.[17] The object, sample no. 4011, showed typical incipient crizzling. Chemical analyses were made of the glass, an electron microbeam probe profile analysis was made of the surface, and several experimental pieces were sawed from the rim and foot.

After the experiments were completed, a few of the sawed pieces were placed in chambers with controlled relative humidities. As reported earlier, when stored overnight at near-zero RH, the glass degenerated dramatically to a severely crizzled state. But it was not then known how low the RH could go without causing degeneration. We now have some further information on that subject. The chamber with the next lowest RH had a level of 12–14%, which was established over a saturated solution of lithium chloride. Before the fragment of glass was placed in this chamber, a series of photomicrographs was taken of its surface. The glass was placed in the chamber on January 31, 1975, and removed on October 25, 1977. (A few casual examinations had been made in the interim.)

It appeared to the author that this glass sample showed somewhat more prominent crizzling after the two years and nine months storage at the low RH than it did at the beginning of the experiment. A microscopic examination was made, and the results were compared to the photomicrographs taken at the beginning. Most of the fissures which could be seen after the storage at low RH were also visible in the original photomicrographs, there being only about a 2–3% increase in the number of fissures. This relatively small increase in the number of fissures would not account for the apparent degeneration toward severe crizzling, but a microscopic comparison between this sample and another sample stored at 70% RH did provide evidence which could explain it. The fissures in the glass stored at the lower RH were noticeably more prominent. They had the appearance of being wider and "more open" than those on the glass which had been stored at the higher RH. Therefore, although storage at the low RH had not appreciably increased the number of fissures in the surface, it had opened them up. Consequently, one must conclude that storage at an RH in the range of 12–14% for two to three years promotes a degree of dehydration, which is dangerous for glass with incipient crizzling.

A Comment on Treatment

Although the corrosion of glasses has been extensively studied, there is not complete agreement upon the details of the chemical mechanism by which the attack of water proceeds.

17. Sample no. 4011, Figure 3, in reference cited in footnote one.

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The mechanism may be complicated and indeed may vary from situation to situation and from one glass system to another. Some knowledge of the details of the mechanisms (or, at least, a working hypothesis about them) is always necessary when attempting to devise treatments for various types of early glasses. This is true for stained glasses and ancient glasses as well as for crizzled glass objects. We have some thoughts on the matter and some experiments to suggest, but, by and large, details of the mechanism can be established and accepted by the community of glass scientists only after a great many experiments on many different glasses under varying and carefully-controlled conditions have been carried out. Such an undertaking is well beyond the scope of our Museum's scientific program, but we wholeheartedly encourage others to pursue such studies.

One point upon which there is general agreement is that the hydrolysis of glasses, their chemical attack by water, results in a depletion of alkali at the affected surface of the glass, and the conversion of the glass into a hydrated state. Numerous experiments, including several done on crizzled objects at our Museum, have confirmed this depletion of alkali.

An important point we wish to make here is in response to a suggestion which has frequently been raised, to the effect that if crizzling is caused by the removal of alkali, why not simply replace the alkali to reverse the process and restore the glass? The problem is that when the alkali is removed and the glass becomes hydrated, the molecular structure of the glass is altered. That is to say, its silicate network, or the "skeleton" of the glass, is also almost certainly disintegrated by the same process that causes the leaching of the alkali. The resulting structure is probably more like that of a hydrated silica gel than that of the original glass. Therefore, simple replacement of the alkali to its original concentration level should not be expected to transform the hydrated material back into a glass any more than the addition of carbon dioxide and water to a piece of charcoal should be expected to transform it back into an oak log. It is the way atoms are bound together—as much as what atoms are present—which determines the physical nature of matter, in this case the glassy character. Therefore, there is little hope, in the author's opinion, that the process of crizzling can be reversed chemically without some high-temperature process which would fuse the surface of the material and reconstitute it into a glass. Because high-temperature treatments are not likely to prove both feasible and effective, we are left only with applications of coatings or impregnations to consolidate a crizzled surface into something resembling its original glassy state.

Until now, most efforts at consolidation have proven unsuccessful in that the resulting appearances of the treated objects have been, if not displeasing, at least not glasslike. It may be that recent research at The Corning Museum of Glass[18] will offer some hope in this regard. Pretreatment of other types of deteriorated glasses with silanes has improved adhesion and penetration of consolidants. Such treatments may allow greater latitude in the selection of consolidants and their means of application to crizzled glasses, so that appearances can be achieved which more closely resemble the original glass surfaces.

A Final Note

As this article was going to press, we had a most informative discussion with Dr. Stolow regarding the construction of a new case to be installed in our existing gallery. This case, which will contain ancient glass, will be controlled with silica gel and will be used as an

18. Unpublished work by Raymond Errett of the Museum staff and Shelley Reisman, then an intern at the Museum, in consultation with Dr. Merrill Lynn of Corning Glass Works.

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experimental installation for the new building. Dr. Stolow made many very helpful suggestions and comments, some of which have a direct bearing on the contents of this article. Readers interested in this subject should watch for his forthcoming publications in the conservation literature.

It will be recalled that in several instances we added water to silica gel by spraying or misting it directly onto the surface with raking. Dr. Stolow does not recommend this procedure for several reasons. First, it can lead to decrepitation of the gel, that is, the gel may break up into smaller particles. This can be a disadvantage in systems where the gel is supported in fabric-covered panels, as the smaller particles fall out more easily; and also, small particles produced by decrepitation may cause dusting. Perhaps the most serious objection to adding liquid water directly to the gel is that it is difficult to add the water uniformly—and this difficulty becomes accentuated when one has to deal with large quantities of gel. In a paper presented at the meeting of the American Institute for Conservation in Fort Worth during June, 1978, Dr. Stolow discussed systems for conditioning silica gel in controlled-humidity chambers.

Dr. Stolow feels that the presence of other water-abundant phases in a system controlled by silica gel can have a beneficial effect by helping the gel to buffer the system, even though it does introduce another variable. He also prefers the use of larger-sized particles in order to prevent their escaping through the fabric covers of panels supporting the gel. Because our trial installation will involve the use of such panels, a mesh size of 3–8 will be used in accordance with Dr. Stolow's recommendation.

Acknowledgements

It would be difficult to list here the names of all those who contributed to this complicated project. The author hopes that those whose names are not mentioned below will accept his thanks anonymously and take satisfaction in knowing their efforts were directed toward a worthwhile cause. Special thanks are due Judy Snyder, who for three years recorded the data and looked after the experimental cases. She also assisted in the preparation of the manuscript. In the later stages of this work, Susan Johnson ably carried out these same responsibilities. Dr. David J. Fischer conducted several preliminary studies which, although they are not discussed in the text, were essential to the project. He was assisted by Joseph Maio, who also helped in maintaining the experimental cases. All too often the efforts of members of museum security staffs go unnoticed, so it is a special pleasure to acknowledge here the willing cooperation of the guards who took data during those times the Museum was closed. They are: William Buchko, Patrick Eldred, Charles Gardner, Harold Gray, Ronald Ogden, Kerry O'Shanick, Walter Schroeder, Deborah Tally, Joseph Turchick, Roswald Viele, and Paul Yorio.

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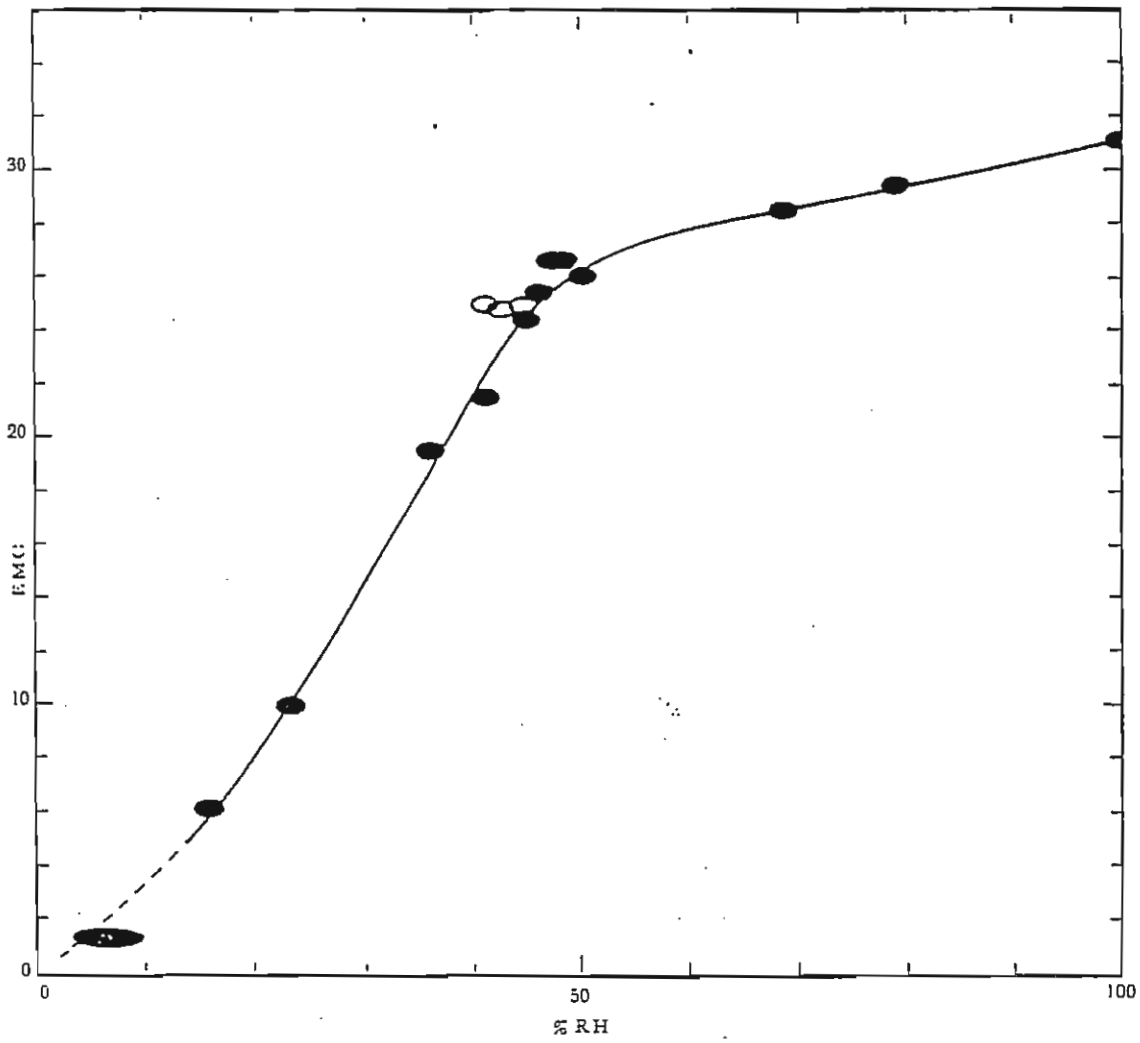

FIG. 1. *Equilibration curve for silica gel used in the Crizzling Case experiment. The curve shows the equilibrium RH of air in contact with prepared samples of silica gel having various moisture contents. (EMC is expressed as percentage of water relative to dry weight of gel.) Hysteresis is not indicated because of the small number of points determined. Open ellipses are data for samples of gel removed from the case at three stages of the experiment.*

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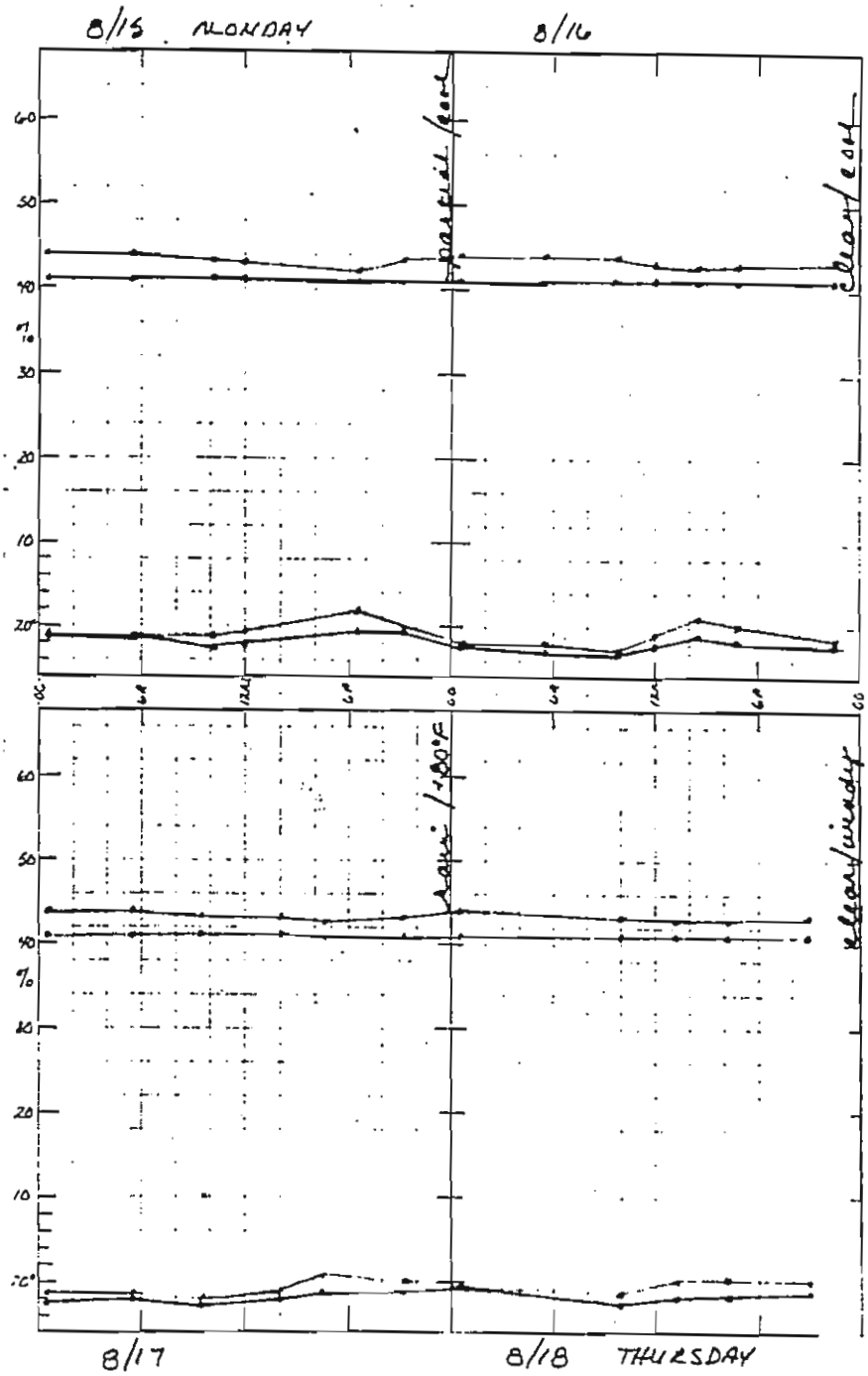

FIG. 2. *Page from Mrs. Snyder's and Mrs. Johnson's daily log book. Data are for four mid-summer days in 1977 and are typical of periods when the Crizzling Case was well stabilized. The plot shows raw data, not yet corrected for a slight calibration difference between the two probes.*

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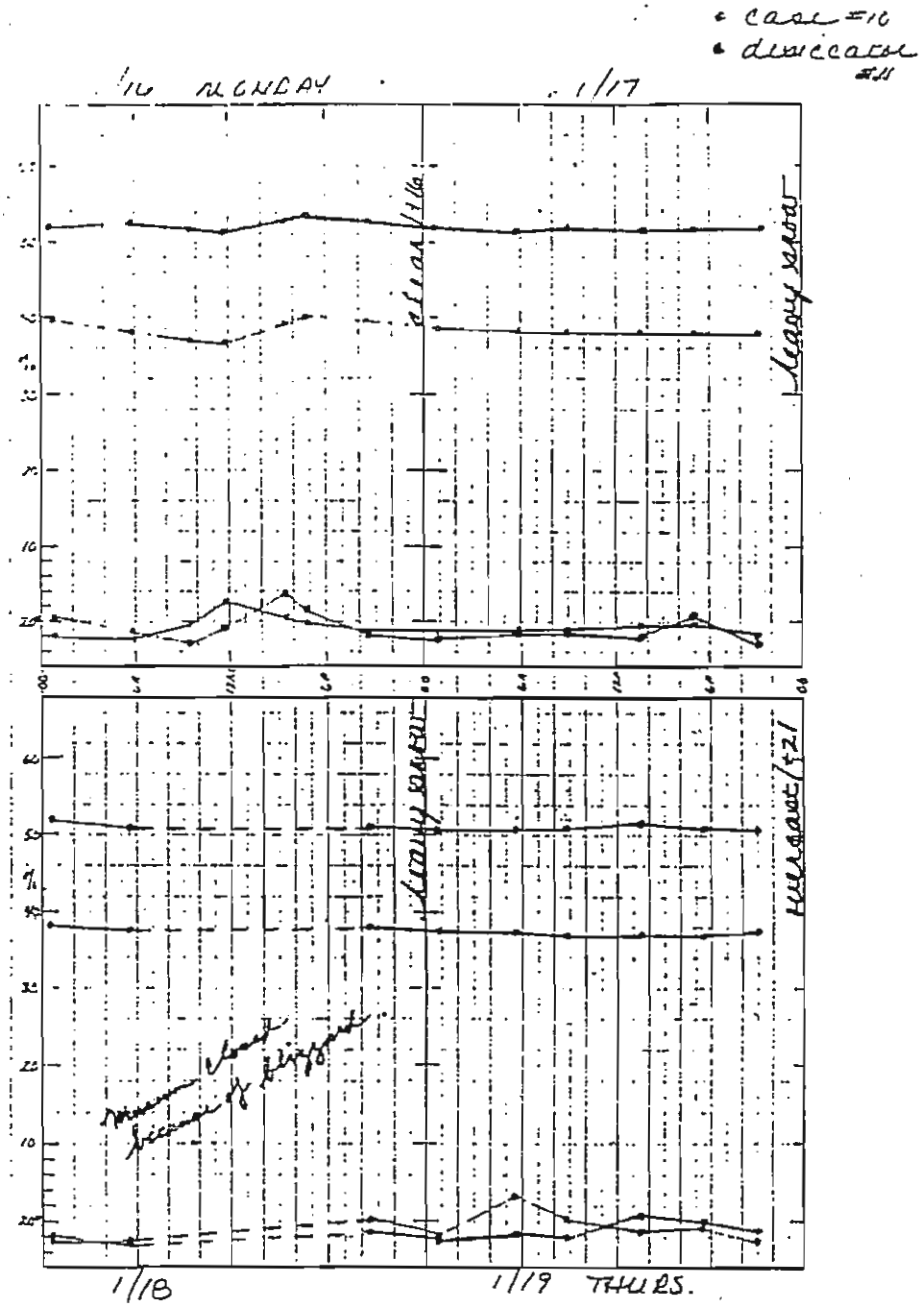

FIG. 3. *Page from Mrs. Snyder's and Mrs. Johnson's log book. Data are for four mid-winter days early in 1978 when there was a heavy snowfall. The lower of each pair of RH curves is for the Crizzling Case while it was drying out exponentially. The upper RH curve is for one of the chambers of silica gel used in establishing the RH* versus *EMC curve (EMC = 26.1%), which was just approaching its equilibrium state. The peaks in the temperature curves at the bottoms of the graphs result from occasional increases in the ambient temperature owing to some peculiarity of the building's heating system.*

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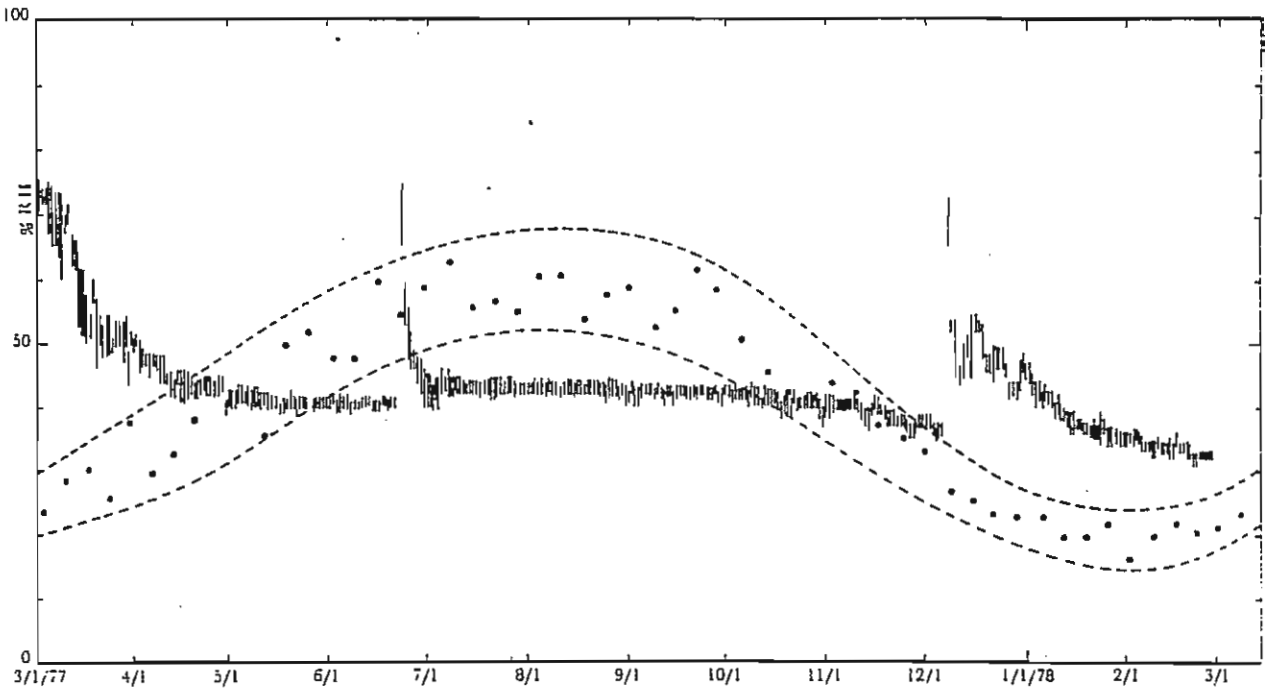

FIG. 4. *One-year RH history of the experimental Crizzling Case plotted as a daily record. RH values measured at two locations within the case are plotted as vertical lines. The length of each line represents the daily range. Additions of water to the system are evident in early March 1977, late June 1977, and early December 1978. In all, some 5000 measurements were used to construct this curve. Solid dots indicate weekly mean ambient RH values immediately outside the case. The broken curves are RH limits which include approximately 95% of the recorded data. The central tendency of RH values measured in a different part of the Museum, the Ancient Gallery, generally falls within the same limits, but the RH tends to wander outside the limits more frequently to temporary extremes of higher or lower RH.*

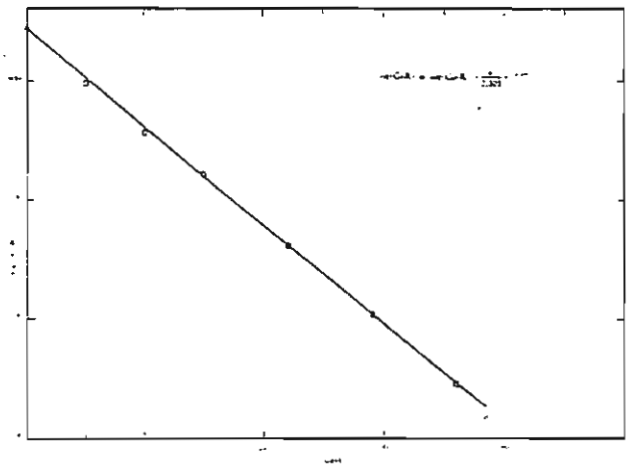

FIG. 5. *Plot of log (C-R) versus time for RH data recorded in the Crizzling Case experiment during the interval December 17, 1977 till January 23, 1978. C is the RH measured within the case at time t, R is the average ambient RH, which is known to have been about 22%, and C_0 is the RH within the case at t = 0. The resulting straight line indicates that the drying out of the case is exponential with time, in accordance with the model proposed by Thomson. From the slope of the line, a rate constant of k = 0.0192 per day was calculated, which yields a hygrometric half-time of 36.1 days.*

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A NOTE ON THE SCIENTIST'S DEFINITION OF GLASS

ROBERT H. BRILL

Introduction

THE objective of this note is to explain for the glass scholar the scientist's definition of glass, and to describe the physical picture that the scientist has in mind when he uses the word "glass." It is important that the scholar be familiar with this picture if he is to understand fully and evaluate the findings reported from time to time by scientists who are investigating ancient glass.

In order to explain this picture clearly it is necessary to review qualitatively the fundamental concepts of the Kinetic Theory and to discuss the viscosity of liquids.

The most significant contributions of the chemist to human knowledge have been his successes in establishing correlations between the experimentally observed properties of matter and his knowledge of its composition and structure. The chemist treats the composition of matter in terms of atoms of chemical elements and the ways in which they combine to form molecules of chemical compounds. He seeks to understand the changes that occur when chemical substances undergo reactions with one another. Of equal significance, however, are the models the scientist has developed which tell us how individual molecules are arranged or interact within matter; that is, how the structure of matter on the infinitesimal scale of the atom accounts for the properties of matter on the scale which we observe in the laboratory and in our daily lives. These findings are summarized in the Kinetic Theory of Matter and will be used here to explain the nature of the three "classical" states of matter—crystalline,[1] liquid, and gaseous.[2]

It can readily be seen that the chemical composition of glass is not the thing that makes glass "glass," since hundreds of thousands of different chemical compositions can be made into glasses. (For example, the files of Corning Glass Works alone contain a bewildering array of some 75,000 different glass compositions.) We must resort instead to an examination of physical structure and atomic arrangements to define what we mean by "glass."

The Kinetic Theory of Matter and States of Matter

The fundamental basis of the Kinetic Theory is that all matter consists of extremely tiny particles, molecules, which are constantly in mo-

1. In modern scientific terminology the word "solid" is taken to mean "crystalline solid."

2. For our purposes the words "vapor" and "gas" may be assumed to be equivalent.

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tion. These individual molecules consist usually of small numbers of atoms held tightly to one another by forces called chemical bonds. The motion of molecules can best be described in terms of a quantity defined as the kinetic energy.[3]

The kinetic energy of a moving object is given (in energy units called ergs) by the following equation: $KE = \frac{mv^2}{2}$, where m is the mass or weight (in grams) and v is the velocity (in cm./sec.) with which the object moves. This equation is known to hold for the largest, smallest and all intermediate material objects in the universe: planets, billiard balls and molecules.

If an object is at rest its velocity is zero, and so, from the defining equation, the kinetic energy also becomes zero. For moving objects, as the velocity, v, increases, the kinetic energy increases rapidly, since it is proportional to the square of v. Doubling the velocity of a moving object increases the kinetic energy by a factor of four; tripling the velocity increases the kinetic energy by a factor of nine. Moving at the same velocity, objects of greater mass have a proportionally greater kinetic energy.

The kinetic energy of any moving molecule is directly proportional to the Absolute Temperature.[4] This means that as the temperature is increased the kinetic energy of molecules is increased, and consequently the velocity with which the molecules are moving is also increased.

At a given temperature the average *kinetic energy* of all molecules is the same, regardless of their chemical compositions or masses. For example, at room temperature, a molecule of water has the same kinetic energy as a molecule of carbon dioxide. From the defining equation then, if the kinetic energies of different molecules are to be equal, it can be seen that the heavier molecules must move somewhat more slowly than light molecules at a given temperature. Despite the fact that molecules move very rapidly, their velocities being of the order of the velocity of rifle bullets, their individual kinetic energies are minute, since their masses are so small. The kinetic energy of a molecule at room temperature is only 6×10^{-14} erg.[5] For comparison, one erg is the approximate energy expended by a mosquito in launching himself into flight.

The kinetic energy of a molecule may be regarded as a measure of its tendency to stay in motion. On the other hand, there are attractive forces which act between molecules and tend to hold them together. The magnitude of the attractive forces depends upon the particular molecules involved, but is independent of temperature. There is a constant competition between the kinetic energy and attractive forces. The relative balance between these forces determines the physical state in which matter exists.

Consider the chemical substance, water. At relatively high temperatures (in excess of the boiling point of 100° C.) the kinetic energy of the individual molecules is rather large and sufficient to overcome the attractive forces. Therefore the molecules move about independently of one another. The water is thus in a gaseous state and constitutes the invisible vapor we call steam. The molecules are separated from one another by distances which are much greater than the size of the molecules themselves. They move about at a great velocity, colliding frequently with one another and the walls of the container. In fact, it is the collisions with the walls of their containers which cause gases to exert a pressure. At higher temperatures the increased kinetic energy of the molecules leads to more energetic collisions

3. A detailed description of the Kinetic Theory will be found in almost any up-to-date textbook of general chemistry on the college level. Most of these treatments should be readily intelligible to readers of this *Journal*.

4. The Absolute Temperature is calculated by adding 273° to the temperature in Centigrade. Room temperature may be taken as about 293° Absolute.

5. $6 \times 10^{-14} = .000000000000006$.

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producing an increase in pressure. This chaotic motion and general lack of interaction between the molecules is characteristic of all matter in the gaseous state.

If the temperature is lowered the water molecules give up some of their kinetic energy, and at temperatures below 100° C. the kinetic energy becomes comparable in magnitude to the attractive forces which tend to hold the molecules together. Physically this means that the molecules must stay close to one another. However, the kinetic energies are still sufficient to keep them moving about. The resulting structure is a liquid in which the molecules move freely, and the molecular arrangement constantly changes from one random configuration to another. The liquid has no mechanical rigidity. This liquid state occupies a much smaller volume than the gaseous state because the molecules have less space between them.

At still lower temperatures (below the melting point of 0° C.) the attractive forces now completely dominate the kinetic energy, and each molecule is held tightly in place, occupying a definite position in a perfectly ordered array. This ordered structure is called a crystal lattice, and may be likened to a three-dimensional checkerboard. The kinetic energy of the molecules here shows up in the form of vibrations of each molecule around the positions they occupy in the crystal lattice.[6] The most important distinction between the liquid and crystalline states is that in a crystal the molecules are arranged in a perfectly ordered fashion, whereas in a liquid they move around in a completely haphazard way and show no semblance of order. In addition, crystals have a mechanical rigidity that is not found in liquids, where the molecules are free to move with respect to one another.

Since the magnitude of attractive forces depends upon the type of molecules involved, each chemical substance has its own boiling point and melting point. Molecules like oxygen (each containing two atoms of oxygen attached together) exert very weak attractive forces upon one another and therefore the melting points and boiling points are very low (—218° C. and —183° C.) Thus oxygen is a gas at room temperature. For substances like iron or silica, the attractive forces holding the individual units in place are very strong and thus the melting points and boiling points are very high. A great deal of thermal energy is required to break the strong bonds that hold the individual units in place.

It should also be noted here that most of the crystalline materials we encounter in our daily lives do not consist of large single crystals. Soil, plaster, concrete and metals, for example, all consist of aggregates of very minute crystals.

Figure 1 summarizes the kinetic pictures and conditions associated with these physical states.

The Glassy State of Matter

Within the three "classical states" of matter, there is no place for glasses.[7] X-ray studies and other physical measurements confirm that although glasses have the mechanical rigidity of crystals, they have the random or disordered structure of liquids. It is therefore necessary to define a fourth state of matter, the glassy state, which combines these two properties. The scientist's definition of a glass, then, is that a glass is a substance in the glassy state, a state in which the molecular units have a disordered arrangement, but sufficient cohesion[8] to pro-

6. If the temperature is lowered still further the kinetic energy continues to decrease and the vibrations become less and less vigorous.

7. There is also no place for many other common forms of matter; for example, wood, rubber, plastics, dough, and living cells, to mention a few.

8. This is admittedly a weak definition from both semantic and scientific viewpoints, since the terms "cohesion" and "rigidity" are in themselves evasive of exact definition, and since no quantitative extent of disorder is prescribed. This description does, however, suit the present purposes of establishing the physical picture of the glassy state.

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Gaseous State

Individual molecules separated from one another by relatively great distances and moving in a completely chaotic fashion. No interaction between molecules except for collisions with one another.

$$KE > A$$

Liquid State

Molecules are held *close* to one another by attractive forces, but are not held rigidly in position. They move about constantly changing from one disordered state to another.

$$KE \sim A$$

Crystalline State

Strong attractive forces hold molecules rigidly in position. Each molecule occupies a definite position in a perfectly ordered three-dimensional lattice.

$$KE < A$$

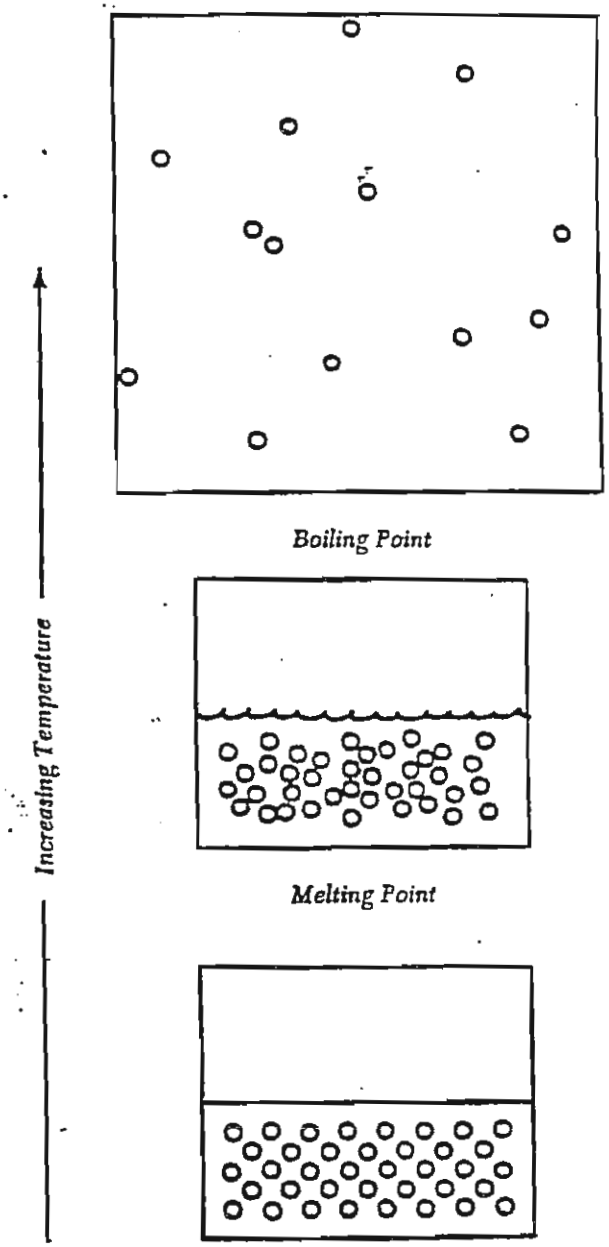

Fig. 1. *Kinetic Models of States of Matter.* The size of the molecules relative to their containers is *greatly* exaggerated. KE represents the kinetic energy of individual molecules and A the attractive forces acting between molecules.

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duce over-all mechanical rigidity. The term "vitreous state" is sometimes used and has exactly the same meaning. Matter of many different compositions may exist in this state.[9] In other words, there is no one substance which is uniquely glass. The word "glass" is a generic term, and we should most properly speak of "glasses" rather than "glass," just as we speak of "metals," "textiles," and "ceramics."

The nature of the glassy state is described[10] in Figures 2, 3, 4 and 5. Figure 2 shows the molecular structure of a crystal of quartz (silicon dioxide; SiO_2). Within quartz, a truly crystalline substance, the individual atoms are arranged in a perfectly ordered fashion. Figure 2 is a two-dimensional, schematic representation of what is really a three-dimensional lattice.[11] The solid dots represent silicon atoms; the open circles are oxygen atoms. They are held together by chemical bonds which are about one hundred times stronger than the attractive forces discussed previously which hold one molecule of water to another.[12] It must be realized that these individual atoms are extremely small, too small ever to be "seen" by any kind of microscope that can be visualized in the framework of our present knowledge of science. If one were to attempt to draw a complete grain of sand, magnifying each atom to the size drawn in these diagrams, a sheet of paper 100 miles long and 100 miles wide would be required.

When a crystal of quartz is heated to high temperatures (approximately 1500° C.) the chemical bonds holding the atoms together are broken. The atoms, or small groups of atoms, collapse into a molten state which has the random, disordered structure of a liquid. Upon cooling, if sufficient time is allowed, the individual atoms or groups of atoms find their way back into a crystal lattice. On the other hand, if the melt is cooled relatively quickly, the atoms do not quite get back into place, and the result is a *glass* of pure silica, as shown in Figure 3. Here the remnants of the quartz structure are still recognizable, but since the ordering is not perfect, one is forced to consider this state of silica as resembling a liquid

9. The insistence of many authors on the inclusion of the word "inorganic" in their definitions of glass seems hard to justify if one takes more than a parochial view of the subject. It evidently stems from a habitual association of "glass" with the more common man-made commercial glasses, but seems to be an unnecessarily restricting viewpoint. Not only do many so-called "organic" materials exist frequently in the glassy state, but the very terms "organic" and "inorganic" seem more and more to take on a peculiar vagueness for which there can be no place in so important a step as defining a fundamental state of matter.

10. This structural model of glasses known as the random network theory, and the two-dimensional method of representation were first used by W. H. Zachariasen, "The Atomic Arrangement in Glass," *The Journal of the American Chemical Society*, Vol. 54, No. 10, October 1932, pp. 3841-3851; and by B. E. Warren and J. Biscoe, "Fourier Analysis of X-Ray Patterns of Soda-Silica Glass," *Journal of the American Ceramic Society*, Vol. 21, 1938, pp. 259-265.

11. In three dimensions each silicon atom is located at the center of a tetrahedron and is attached to four oxygen atoms which are located at the corners of the tetrahedron. The tetrahedra are arranged symmetrically in space so that each oxygen atom occupies a corner of two different tetrahedra. The geometrical angle formed by a silicon atom and any two oxygens attached to it is 109°. The angles formed by the oxygen atoms and the two silicons they bridge are all exactly alike and about 145°. Although each tetrahedron appears to have a composition of SiO_4, the over-all composition of the crystal is SiO_2, since each oxygen atom is shared by two tetrahedra.

Because of the difficulties of drawing a two-dimensional representation of these structures, Figures 2, 3, 4, and 5 are somewhat deficient in oxygen atoms as required by the rules of chemical valency. In Figure 6 the correct number of oxygen atoms is included. Actually all oxygen atoms should be attached to silicate chains and those oxygen atoms which are not should be visualized as protruding upward or downward from silicon atoms above or below the plane of the paper.

12. For those readers who are familiar with chemical bonds the Si-O bond should not be considered to be either a completely covalent bond in which the bonded atoms share the valence electrons equally or a completely ionic bond in which Si^{++++} and O^{--} ions are held together by electrostatic attraction. Actually the nature of the Si-O bond lies somewhere between these two extremes, having perhaps 50 per cent ionic character. The individual atoms really should be drawn with larger radii, so that they are in contact with one another, but this would obscure somewhat the structural arrangement.

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more than it resembles a crystal. This, however, is somewhat inconvenient, since the resultant glass is clearly different from "ordinary" liquids in that it has a rigidity approaching that of crystals. In addition, the network does not really resemble closely the structure of conventional liquids, which consist of much smaller molecular units. Thus we can see again the need for the definition of a fourth state of matter called "the glassy state."

Actually, it is more satisfactory to relate glasses to the broader concept of the "polymerized state," since this more general term would allow glasses to be classified with other materials such as plastics, rubber, and dough. The "polymerized state" refers in general to materials which have disordered molecular structures consisting of long chain molecules more or less entangled with one another. The individual molecules may contain tens of thousands of atoms. In the case of materials like rubber or soft polyethylene, the individual chains are very flexible, accounting for the over-all rubbery elasticity of the materials. The glassy state may be regarded as a special case of the polymerized state in which the individual chains constituting the material have in themselves great rigidity. This rigidity usually results from a high degree of cross-linking between the chains which joins them together to form a complex network, or it may result from attractive forces holding together adjacent segments of neighboring chains. In general, all polymerized materials, such as rubber, if cooled sufficiently, will undergo a transition into a glassy phase below temperatures where the individual molecular chains lose their "flexibility." The transformation is marked by a change from a viscous rubbery state into a brittle state. The situation is analogous to the freezing of ordinary liquids in that the molecular vibrations which keep the chains wriggling and flexible gradually succumb, as the temperature is lowered, to whatever attractive forces exist. Many plastic materials such as polymethacrylate resins are in a glassy state at room temperature.

Figure 4 shows a two-dimensional representation of a crystal lattice of sodium disilicate.[13] In this crystal, the cross-hatched circles represent sodium ions[14] which are interspersed in a regular fashion between the silicate chains. If this crystal is melted, it also collapses into the random structure of a liquid, and if cooled slowly can be restored to its original crystalline structure. Relatively fast cooling, however, will trap the atoms in a glassy structure such as that shown in Figure 5 before they are able to arrange themselves in a perfect crystalline pattern.[15]

The description of glass given above says nothing about chemical composition because, as was mentioned before, the number of possible compositions of glasses is indefinitely large. Chemical composition does, of course, greatly affect the physical and chemical properties of glasses. In Table I are shown compositions of several familiar glasses. The first is a modern soda-lime glass, which contains about 74 per cent silica (SiO_2), 16 per cent soda (Na_2O), and 5 per cent lime (CaO). The use of soda (or potash) permits the fusion of the silica at temperatures considerably below its

13. The structure is highly schematic and is not at all intended to be an accurate representation of the crystal structure.

14. Sodium ions are sodium atoms bearing a positive electrical charge. They are aligned adjacent to oxygen atoms bearing negative charges and thus preserve the over-all electrical neutrality of the crystal.

15. An alternative physical model for glasses preferred by some scientists is that glasses consist of aggregates of *extremely* minute crystalline regions, or microcrystallites, which have perfectly ordered lattices but which are themselves randomly arranged and connected by or imbedded in a disordered matrix. This picture and the supporting evidence is presented in a paper by E. A. Porai-Koshits and N. S. Andreyev, "Low-Angle X-Ray Scattering by Sodium Borosilicate Glasses," *Journal of The Society of Glass Technology*, Vol. XLIII, 1959, pp. 235T-261T, and in other more recent publications which are not as readily available to English speaking readers. The refined experiments which might tell which picture is more nearly correct have not yet been possible.

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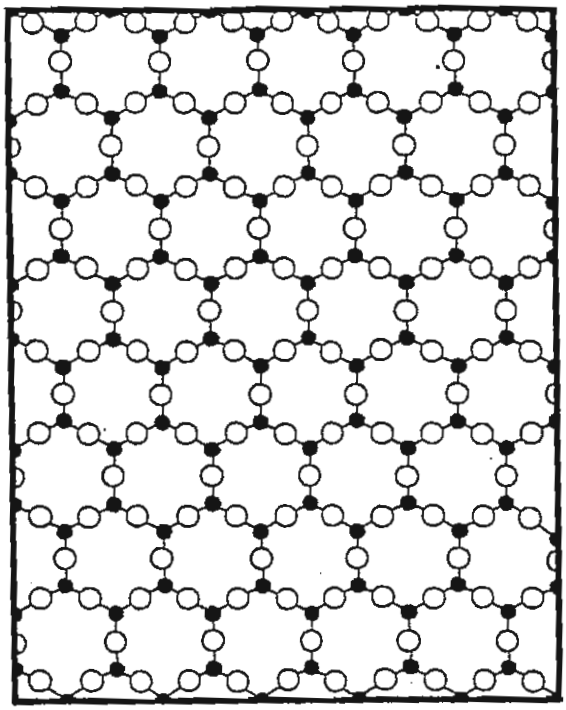

FIG. 2. *Quartz Crystal.*

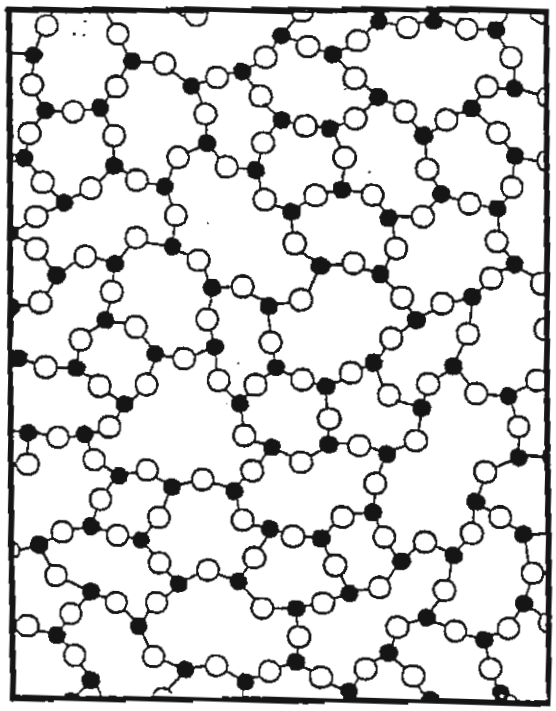

FIG. 3. *Fused Silica Glass.*

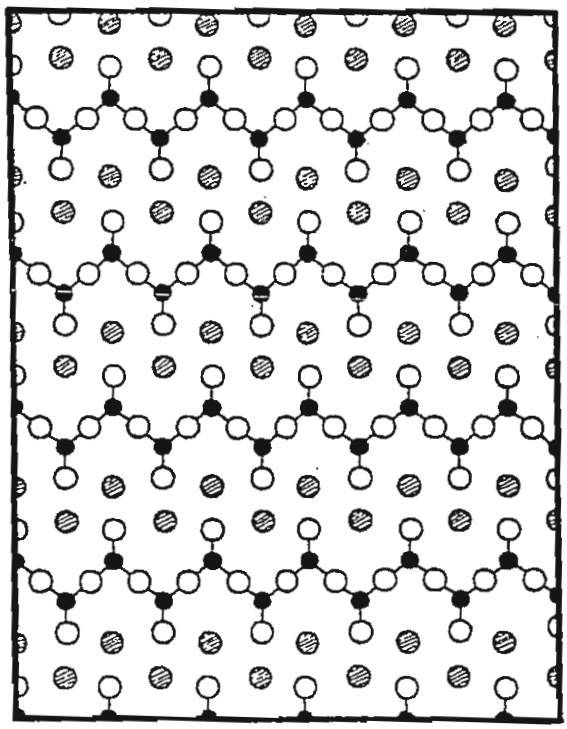

FIG. 4. *Sodium Disilicate Crystal.*

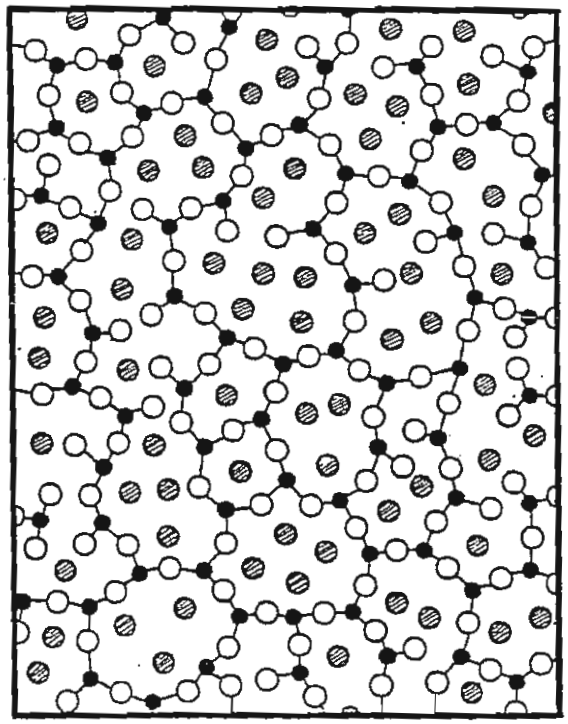

FIG. 5. *Soda-Silica Glass.*

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TABLE I. *Glass Compositions.*
(In Weight Percentages)

		Modern Soda-Lime-Silica	*Typical* Roman*	*Typical Baking or Laboratory*	*Optical High Lead*	*96% Silica*
Silica	SiO_2	73.6%	67.0%	80.5%	35.0%	96.5%
Soda	Na_2O	16.0	18.0	3.8	—	—
Potash	K_2O	0.6	1.0	0.4	7.2	—
Lime	CaO	5.2	8.0	—	—	—
Magnesia	MgO	3.6	1.0	—	—	—
Alumina	Al_2O_3	1.0	2.5	2.2	—	0.5
Iron Oxide	Fe_2O_3	—	0.5	—	—	—
Antimony Oxide	Sb_2O_3	—	1.5	—	—	—
Manganese Dioxide	MnO_2	—	0.5	—	—	—
Boric Oxide	B_2O_3	—	—	12.9	—	3.0
Lead Oxide	PbO	—	0.01	—	58.0	—
		Physical Properties				
Density in gm./c.c.		2.47	2.544	2.23	4.28	2.18
Coefficient of expansion (0°-300° C.)	$\times 10^7$/° C.	92.0	103.4	32.5	91.0	8.0

*Experimental melt based on average composition of many Roman glasses. This composition very closely approximates that of the inlaid plate from Athens described in this *Journal* on pp. 37 through 47.

ordinary melting point. The addition of lime produces a glass which is less prone to attack by water. (Soda-silica glasses are quite soluble in water. Solutions of this material constitute the familiar substance "water glass.") For comparison, the chemical composition of a typical Roman glass is also given. It is apparent that the three principal ingredients in this soda-lime-silica glass are comparable to those in modern glasses. However, the ancient glasses generally contain fairly large quantities of impurities which were introduced from impure raw materials and low quality refractories. Figure 6 is an attempt to show the exceedingly complicated molecular structure of a glass with this composition. It should be borne in mind that the actual structure of the glass network extends in three dimensions.[16]

16. In three dimensions the glassy state of silica may be pictured as an assembly of SiO_4 tetrahedra which are arranged in an irregular or random fashion without the perfect symmetry of the quartz crystal.

This diagram also points out the action of coloring agents. The presence of 2.0 per cent by weight of copper oxide in a glass is sufficient to confer a strong blue color. As shown in the diagram this concentration is represented by only two copper atoms out of the 370 atoms in the portion of the glass represented. As few as one cobalt atom per 3700 atoms of a glassy matrix will color the glass an even deeper blue. This corresponds to a *weight* concentration of only 0.1 per cent.

One of the important distinctions between glasses and crystals is that crystals have very sharp melting points. A crystalline material remains completely rigid up to a precisely defined temperature, at which point it goes over abruptly into the liquid state. The reason for the sharpness of the melting point is that all of the chemical bonds within the crystal are identical and therefore they all break at the same temperature. In the case of a glass, however, where the chemical bonds have been distorted to

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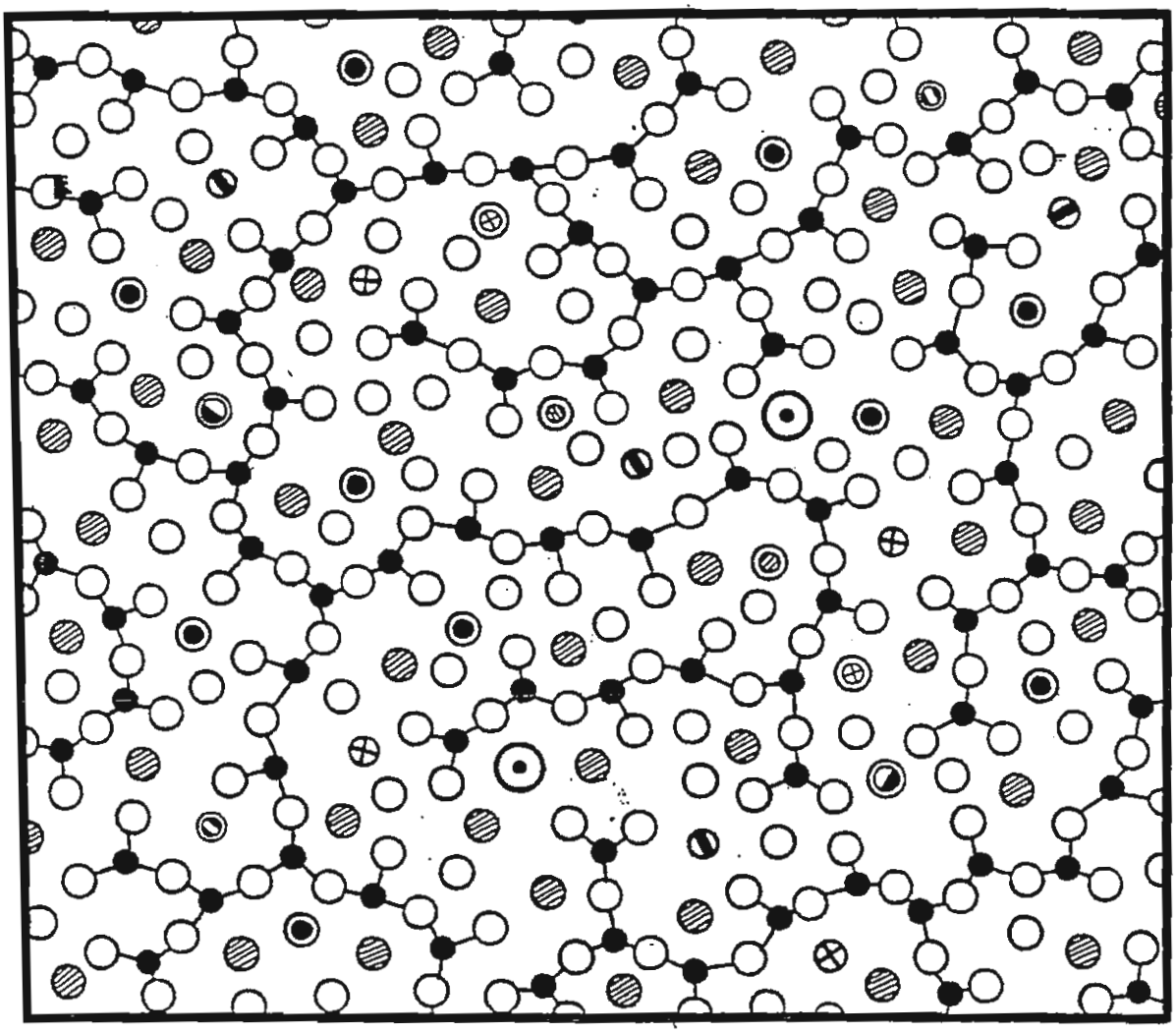
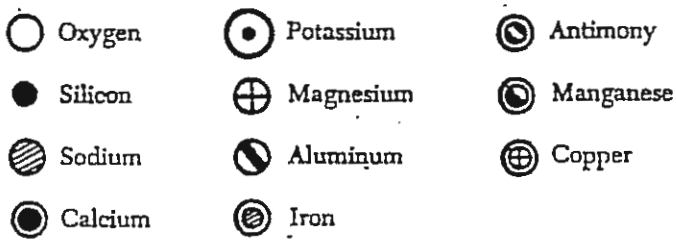


FIG. 6. *Typical Roman Glass.*



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varying degrees from their natural and stable geometrical configurations[17] the different chemical bonds will break at different temperatures. In effect, each chemical bond has its own melting point since each will have its own degree of strain. (The greater the strain the weaker the bond.) Therefore, glasses, instead of having sharp melting points, soften gradually as the temperature is raised (as the weaker bonds break), until at high temperatures they finally become quite fluid. It is this gradual softening over a range of several hundred degrees centigrade which makes it convenient to describe glasses in terms of viscosities.

The Viscosity of Liquids and Glasses

The term "viscosity" is usually applied to liquids, and means, in a qualitative sense, the resistance that a liquid offers to flow. A liquid with a high viscosity such as molasses, will flow at a very slow rate, whereas water, with a considerably lower viscosity, will flow much more readily. Viscosities are expressed in a unit called the poise.[18] The viscosity of water at room temperature is .010 poise; that of SAE 30 motor oil is about 1.0 poise. The viscosity of most glasses at room temperature is about 10^{19}-10^{22} poises,[19] which is about as high a viscosity as can be measured. As the temperature of a piece of glass is raised, the inflexible molecular network breaks down into somewhat smaller units, and the viscosity gradually drops to the order of 10^7 poises, in which region the glass may become deformed under its own weight. At still higher temperatures the viscosity drops to 10^{3-4} poises, under which conditions the glass will flow quite readily into a mold, or can be blown with ease. When heated to very high temperatures, the viscosity of glasses may be so low that they become as fluid as thin motor oil.

Figure 7 shows the dependence of viscosity on temperature for the glasses in Table I. For comparison, the viscosities of several familiar substances *at room temperature* are marked on the scale.[20] It should be noted especially that an increase of one unit in the exponent of 10 on the vertical scale corresponds to a ten-fold increase in the viscosity of the glass.

A number of particular points on the viscosity-temperature curve have been defined by glass scientists for their own convenience in comparing glasses of different compositions. For example, the softening point of a glass is that temperature at which the viscosity is $10^{7.65}$ poises.

At some point between the two extreme viscosities mentioned, glasses may be considered to change from the "glassy state" as described above, to a true liquid state, where the molecular units are small and the glass flows readily. There is no clear-cut point of transition, however, and any attempt to define one would be arbitrary at best. This apparently is why so many scientists prefer to consider glasses, even at room temperature, to be extremely viscous liquids, and to describe them as "under-cooled liquids."

Theoretically it should be possible to convert any liquid into a glass if it could be cooled rapidly enough to a sufficiently low temperature. In reality, however, it is only those liquids which are quite viscous at their freezing points that go easily into the glassy state. As with so many other scientific phenomena this can be explained qualitatively in terms of the physical pictures of the molecules involved. Those

17. See footnote 11 on the structure of quartz, and compare Figures 2 and 3.

18. Named after J. L. M. Poiseuille, the 19th century scientist who worked out much of our present knowledge concerning liquids.

19. The shorthand notation 10^{20} (10 to the 20th power) means 1 followed by 20 zeros. In the same notation, $10^3 = 1{,}000$ and $10^6 = 1{,}000{,}000$.

20. Two of the values on this table were taken from G. E. Alves and E. W. Brugmann. "Estimate Viscosities by Comparison with Known Materials," *Chemical Engineering*, Vol. 68, No. 19, September 18, 1961, p. 182.

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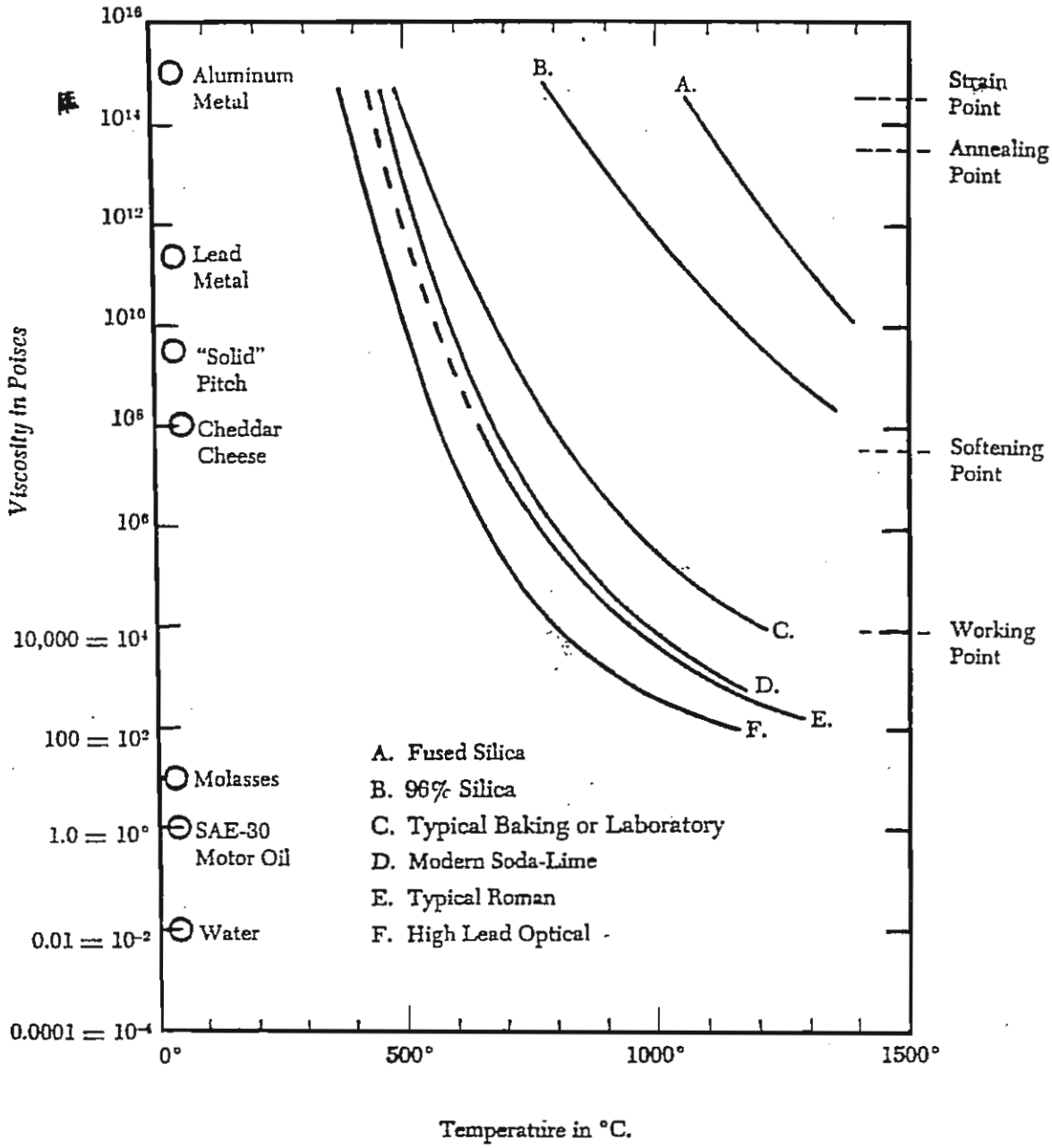

FIG. 7. *Viscosity-Temperature Curves for Several Glasses.*

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liquids which have high viscosities such as melted silica, usually consist of rather large molecules. These large molecules tend to become very much entangled with one another and thus can flow only with difficulty. It is reasonable to expect that such liquids should form glasses readily since it is difficult for large, cumbersome molecules to arrange themselves into a crystal lattice. At ordinary rates of cooling they are likely to be "frozen" into a rigid (or very viscous) glassy condition before crystallization can occur. In the case of melted mixtures of soda, lime and silica the organization of the different kinds of molecules into one or more crystal lattices simultaneously is quite clearly a very complicated process.

Liquids having smaller and simpler molecular structures, such as water, have correspondingly lower viscosities and even at very rapid rates of cooling can still manage to become organized into perfect crystal lattices before becoming completely rigid. Such liquids, therefore, do not ordinarily exist in the glassy state. With very rapid rates of cooling and carefully controlled conditions, however, some familiar liquids of low viscosity, such as ethyl alcohol[21] can be converted into a glassy state, and the deposition of water vapor onto very cold surfaces (—100° C.) can produce a glassy state of water.[22]

In summary it may be said that to the scientist the word "glass" has a special meaning and that a very definite physical picture is associated with the glassy state. This state is characterized by a disordered molecular structure similar to that of liquids and a mechanical rigidity corresponding to that of crystalline materials.

Because of this physical structure, the mechanical properties of glasses, particularly the "rigidity," change over a wide range depending upon temperature. It is convenient to describe this behavior in terms of viscosity.

The viscosity-temperature relationship varies for glasses of different chemical compositions. A study of these relationships may be useful for learning more about the technological processes used by glassmakers in the past. One example of an application of this type of reasoning appears elsewhere in this *Journal* in an article on an inlaid plate from the Agora.

Another related topic of concern to the glass scholar and archaeologist is the meaning of such terms as frit, paste, faience, enamel, glaze, etc. Although some efforts have been made to define these terms, it is apparent that a considerable amount of confusion still exists as to the meanings of at least some of these words and the distinctions (where they exist) between the materials being described. There are probably as many different sets of definitions as there are people using the terms and one is never quite certain as to just what meaning authors have in mind.

Equipped with an understanding of the nature of glasses and crystalline substances, it should be possible for us to classify intermediate materials into a few (hopefully) distinct categories by employing straightforward structural descriptions of the materials most often encountered.

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21. H. J. de Nordwall and L. A. K. Staveley, "The Crystallization of Vitreous Water and Heavy Water," *Transactions of The Faraday Society*, Vol. 52, 1956, pp. 1061-1066; and "The Formation and Crystallization of Simple Organic and Inorganic Glasses," *ibid.*, pp. 1207-1215.

22. J. A. Pryde and G. O. Jones, "Properties of Vitreous Water," *Nature*, Vol. 170, October 25, 1952, pp. 685-688.

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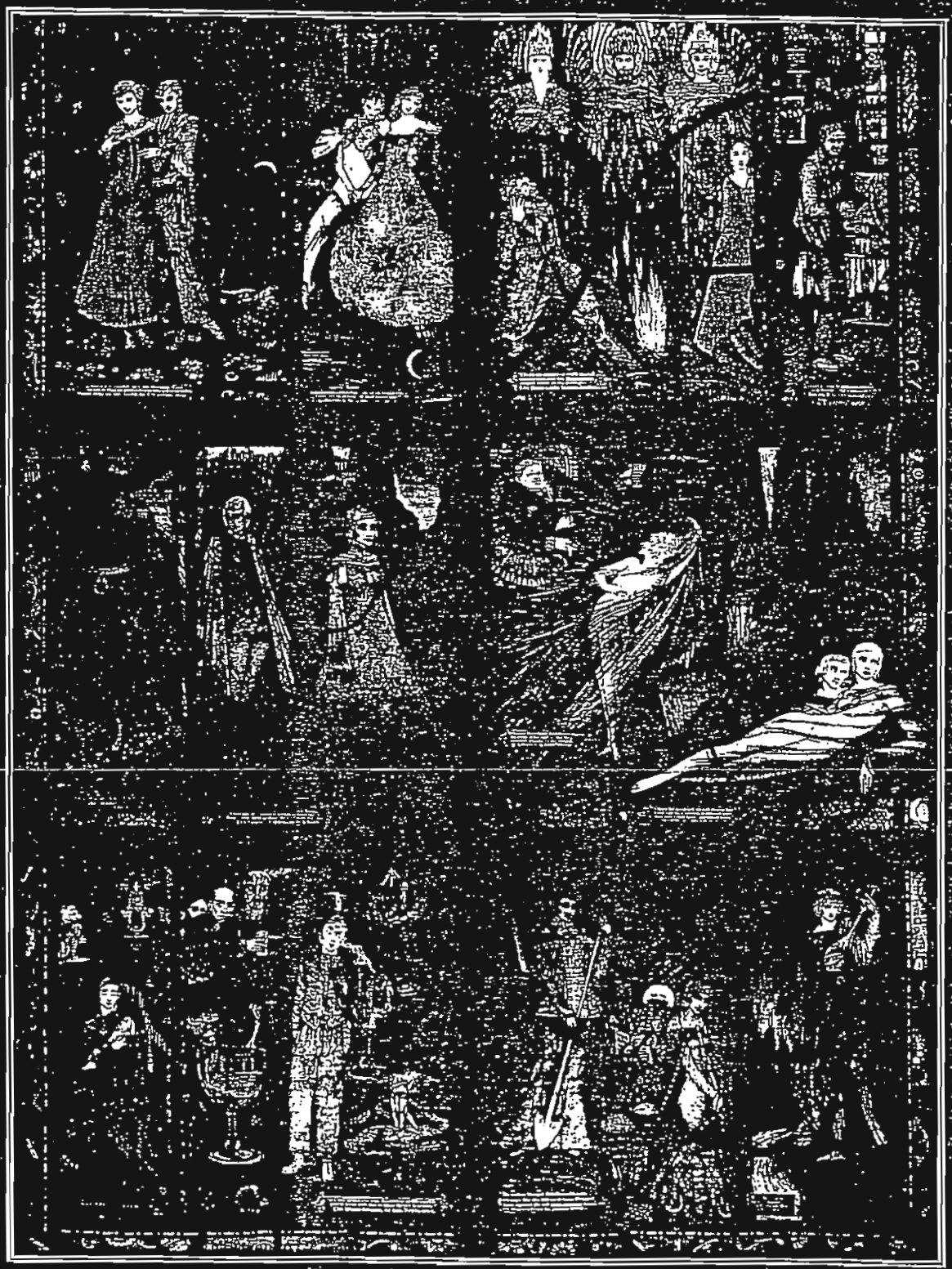

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Harry Clarke and His Geneva Window

by Mary Clerkin Higgins

History

In 1926, the government of the Irish Free State approached one of that country's foremost artists, Harry Clarke, to commission a stained glass window for the offices of the International Labour Conference of the League of Nations in Geneva. Clarke was 36 years old at the time and at the height of his career. He was known internationally for his intense, detailed and imaginative stained glass designs, as well as for his often macabre and bizarre book illustrations. His work, Symbolist in nature, showed a great originality in composition and a masterful use of color.

The Geneva Window (*Figure 1*) was to be an official gift from Ireland to the League. Clarke traveled to Geneva to examine the site and suggested a suitable location in a stairwell. The government left the choice of subject matter to Clarke, who decided upon modern Irish literature, and with the help of friends Lennox Robinson, William Butler Yeats and others, he selected 15 writers and works to illustrate: *The Wayfarer* by Patrick Pearse, *The Story Brought by Brigid* by Lady Gregory, *Saint Joan* by George Bernard Shaw, *Playboy of the Western World* by John Millington Synge, *The Others* by Seumas O'Sullivan, *The Demi-gods* by James Stephens Juno, *The Paycock* by Sean O'Casey, *The Dreamers* by Lennox Robinson, *The Countess Cathleen* by William Butler Yeats, *Mr. Gilhooley* by Liam O'Flaherty, *Deirdre* by George Russell (known as AE), *A Cradle Song* by Padraic Colum, *The Magic Glasses* by George Fitzmaurice, *The Weaver's Grave* by Seumas O'Kelly, and *On Music* by James Joyce.

Work did not begin on the commission until the end of 1927, then progressed very slowly, due to Clarke's numerous other commitments for windows and book illustrations, as well as to the administration of the family stained glass studio and decorating firm. Even worse, Clarke was battling a progressively deteriorating case of tuberculosis. In March, 1929 his doctors insisted that he travel to a sanatorium in Switzerland for convalescence, returning to Dublin over a year later, in May of 1930, to complete work on *The Geneva Window*. It was ready for viewing by September when President Cosgrove of Ireland and other officials came to examine it.

Immediately, President Cosgrove had misgivings. He wrote Clarke, saying that "For several reasons I consider that it would not be desirable to include the panel which contains a representation from the books of Mr. Liam O'Flaherty." His objection to the panel of semi-nude Nelly dancing before Mr. Gilhooley (*Figure 2*) may have been both to the imagery and to the fact that some of O'Flaherty's work was banned at that time by the Censorship Board. His objections grew and he soon wrote Clarke that, "the inclusion of scenes from certain authors as representative of Irish literature and culture would give grave offence to many of our people."

He was hardly alone in that opinion, for as an interview with Mr. R.C. Ferguson, the Secretary of the Department of Industry and Commerce at the time and one of the first officials to view the window, reveals, it was felt by many government officials that "Nakedness was something they were prepared to accept as an artistic requirement, but never nakedness which so suggested sex.... What harm if this window could be smuggled out to Geneva—but there would be no avoiding the opposition of politicians, churchmen and the newspapers. A nation famed as a Catholic stronghold was to be represented as a bizarre almost viciously evil people steeped in sex and drunkenness and, yes, sin." (*Figures 3, 4, 5*) Politically, there was no possibility that the government would send the window to Geneva.

Harry Clarke, still in fragile health and not disposed to compromise on the window, returned to Switzerland in October, immediately after the viewing, and died there three months later. Officially, the government never said outright that it was abandoning the project; indeed, they paid the agreed sum, in full. However, panels were collected, temporarily went on display, and were then put in storage. Clarke's widow, Margaret, was very unhappy with the commission's outcome and tried in vain either to get the government to send the window to Geneva, which she knew would probably never happen, or to sell it back to her. In 1933, after the installation of a new government, she was allowed to buy the ensemble back for the amount originally paid. The window remained in the family until 1988 and, for part of that time, it was on extended loan to the Hugh Lane Municipal Gallery in Dublin.

continued on page 19

Figure 1: The Geneva Window. *Harry Clarke, 1930, 75" x 41". Before Restoration. The restored window will be unveiled during the Wolfsonian's inaugural exhibition in January 1995.*

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In 1988, the family sold the window to collector Mitchell Wolfson Jr. It is to be on permanent exhibition in the Miami, Florida headquarters of the Wolfsonian Foundation, (*Figure 6*), as soon as construction for the new museum facility is completed in 1995. It will be part of the Foundation's inaugural show, 'The Arts of Reform and Persuasion, 1885–1945.'

While much of the show will travel to sites around the United States, Europe and Japan, *The Geneva Window* will remain in Miami Beach. The Foundation is dedicated to "furthering scholarship, conservation, preservation, education and appreciation of the art and history of the period 1875–1945." As its name suggests, this important and fascinating collection concentrates on the decorative and propaganda arts; that is, art that was not made solely for arts' sake.

As with the rest of the history of this window, its sale was also controversial. By allowing this powerful and historic piece to be purchased and sent overseas, lost to Ireland forever, Brian Fallon remarked in *The Irish Times* that, "We have, quite simply, disgraced ourselves again."

Technique

Although Clarke was not the first to employ the techniques used in *The Geneva Window*, he was a recognized master of them. The entire ensemble is double-plated, with the two pieces of glass held in a single lead, one directly behind the other. Plating is often used to obtain a greater richness and depth of color, or to tone a color. In Clarke's hands, it was used to obtain a much greater variety and intermixture of color.

Most of the glass in the ensemble is flashed. When the glass is still a molten gather, a thin layer of one color is placed over and attached to a thicker layer of another color. This gather is then blown into a cylinder and subsequently flattened into a sheet of glass. Most antique red glass is flashed. Any color however, can be flashed and a whole range of combinations can be achieved—red over clear, red over blue, blue over yellow, and so forth.

By the fifteenth century, it was realized that a craftsman could remove the layer of flash by abrasion with a sharp tool to reveal the base glass below—a very labor intensive process, enabling the artist to have two colors on one piece of glass without a necessary lead line. In the nineteenth century, hydrofluoric acid was used to remove the layer of flash, making it possible to eliminate all or only a part of the flashed layer, depending on the amount of time the glass was exposed to the acid, as well as allowing for much more subtle and varied tones of color than were possible with abrasion.

Figure 2: 'Mr. Gilhooley,' by Liam O'Flaherty.

(above) Figure 3: 'Deirdre,' by George Russell (known as A.E.)

Figure 4: 'The Others,' by Seumas O'Sullivan.

With *The Geneva Window*, any area that was not to be touched by the acid was protected with a wax resist, while areas to be acided were left uncovered. The glass was either dipped into the wax with some wax then being removed, or hot wax was applied very precisely with a pen. The glass was then placed in a hydrofluoric bath until the proper amount of flash was removed. Clarke would do this as many as six separate times, adding or removing wax resist along the way, in order to obtain many intricate details and various shades of color down to the base, on the one piece of glass.

In the scene from 'Juno and the Paycock' (*Figure 7*) we see the two layers of glass plating side by side. In *Figure 8*, the two layers are stacked as they would be in the leads. Both the front and back layers have been acided and the varying depths of color can be clearly seen. The deepest shade of color was completely protected during the aciding procedure: the clear areas indicate where the flashed layer has been completely removed, revealing the color of the base glass. Aciding with hydrofluoric acid is a very hazardous procedure necessitating a great deal of care and skill, especially for aciding as detailed as this (*Figures 9, 10, 11*).

After the glass was acided, it was painted using silver stain and vitreous paint. The silver stain consists of a silver salt applied to the glass. Upon firing in a kiln, it forms a colloidal

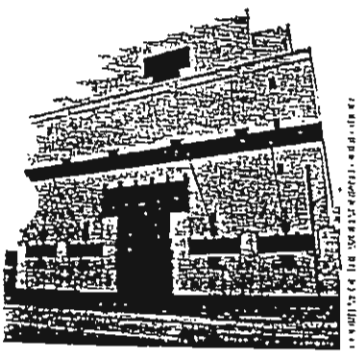
Figure 5: 'The Magic Glasses,' by George Fitzmaurice.

dispersion within the glass, actually staining the glass from a pale yellow to a rich rust color, depending on the amount of silver stain applied, the ability of the base glass to accept the stain and the temperature of the kiln.

For Clarke, the silver stain meant he could add approximately three shades of yellow to clear areas, plus the mixture of the yellow with whatever his base color was, again increasing his palette. This ingenious use of techniques yielded him a very rich mixture of colors.

Vitreous paint is a mixture of a soft, ground glass flux and metallic oxides. After its application, the glass is fired in a kiln at approximately 1200° F, at which point the soft glass flux fuses to the heat-softened base glass, and holds the metallic oxides in place on the base glass. The vitreous paint was used to add the details and to regulate the amount of light coming through the glass. Clarke employed both a pen and a brush to apply the trace lines. He also used overall mattes, frequently stippled with a stiff brush and worked with a needle. Clarke worked with the vitreous paint much as he did with pen and ink for his illustrations. His painting is very detailed, and by using the pen, he was able to get crisper lines without needing to cut back and straighten, as he would have to do had he used a brush.

Figure 6: The Wolfsonian Foundation Building, Miami Beach, Florida



(left top) Figure 7: 'Juno and the Paycock,' by Sean O'Casey. The two layers of plating, side by side.

Figure 8: 'Juno and the Paycock,' by Sean O'Casey. The two layers of plating, stacked.

Conservation

The most immediate conservation concern was the repair of any new breaks in the glass. With stained glass conservation, there is usually the additional concern of what to do with any previous repairs. The traditional method of repair has been either to cover a break with a lead flange or, more frequently, to insert an 'H' shaped lead came between the pieces of broken glass. This often entailed grozing, or removing some of the original glass to accommodate the thickness of the heart of the lead. Fortunately, none of the breaks in *The Geneva Window* had been grozed. Some cracks were new and had not been addressed, three cracks had been glued with what appeared to be a conservation quality epoxy, and two cracks had been covered at some point, after fabrication, with a lead flange.

There were also a number of original cover flanges on the panels. It was possible to distinguish original cover leads from later ones by their appearance. The originals were done in the same gauge lead as the rest of the panel, and their joints were soldered in the same manner as those on the rest of the lead network.

Glass which has been deeply acid etched and is then painted and fired at a high temperature in a kiln has numerous stresses in it which are sometimes resolved by the glass breaking, either in the kiln or at some later time. It was apparent that a number of pieces broke before the ensemble was finished, and rather than redo the many steps of production in areas where the breaks were not considered intrusive, Clarke decided to simply cover the breaks with flanges. At other times Clarke would redo pieces which had broken in the kiln.

All of the original flanges were left in place. The non-original flanges, however, were removed, because they had not been seen and accepted by Clarke and his assistants (*Figure 12*). Because of the internal stresses from the etching and firing, these pieces had sprung, meaning that they no longer lined up perfectly at the crack, leaving gaps between the two pieces which now had to be filled. This usually does not happen when the glass has been either painted or etched, but the combination of etching and then firing increases the stresses and causes the condition to occur.

Because the pieces were etched, the color fluctuated greatly across the length of the crack and the tinted fill material had to also jump from color to color, as necessary. In this case, the material had to fill, as well as hold, the glass together. HXTAL, a conservation quality epoxy, was used

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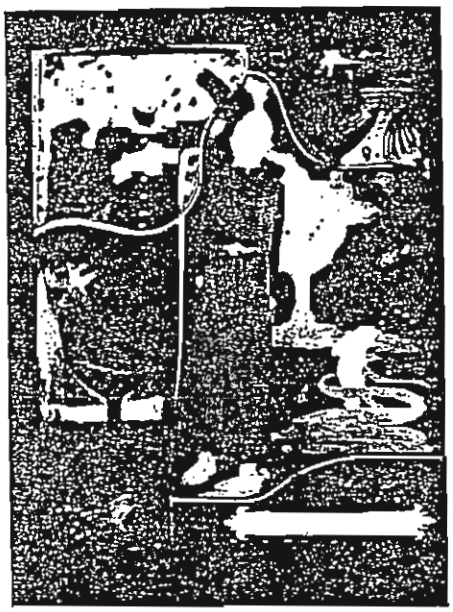
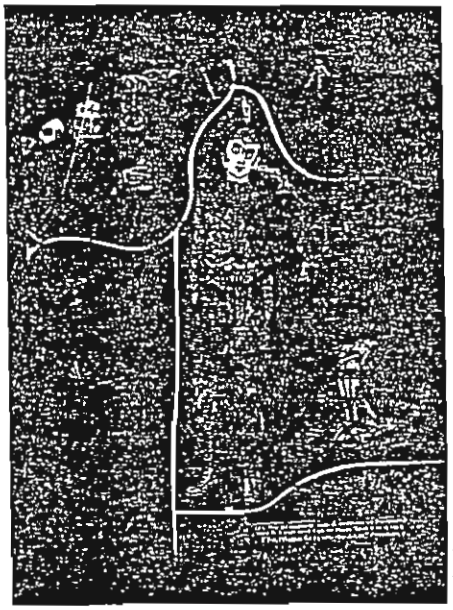
(below left to right)
Figure 9: 'The Magic Glasses,' by George Fitzmaurice. The back layer of plating, etched only.

Figure 10: 'The Magic Glasses,' by George Fitzmaurice. The front layer of plating, etched and painted.

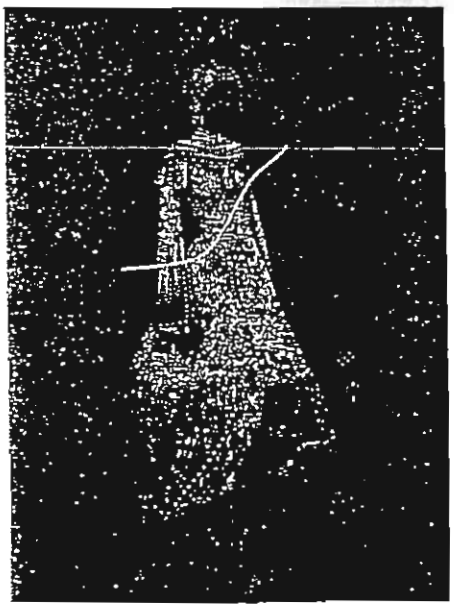
Figure 11: 'The Magic Glasses,' by George Fitzmaurice. The two layers of plating together.





(right) Figure 12: 'The Countess Cathleen,' by William Butler Yeats. Before Gluing.

(far right) Figure 13: 'The Countess Cathleen,' by William Butler Yeats. After gluing and overpainting.



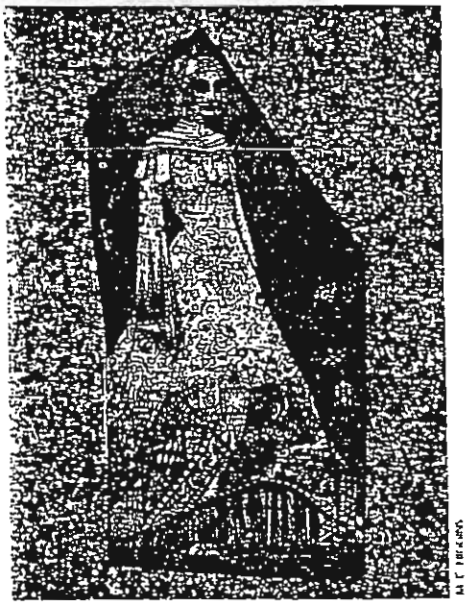


Figure 14: 'On Music,' by James Joyce. After initial gluing.

Figure 15: 'On Music,' by James Joyce. After infill and overpainting.

continued from page 22

for the fills and for any new breaks. It was chosen because it is water-white, has an acceptable match of the refractive index of the stained glass and has held up well in various aging studies of adhesives. The epoxy was then overpainted (*Figure 15*) with cold, or unfired paint, to match the original vitreous paint.

There was one hole in Panel #8, near the head of the minstrel (*Figure 14*), which had been filled in with an opaque brown material. This has now been replaced with a new fill consisting of a thin layer of purple, backed by a thicker layer of lightly tinted HXTAL, to match the flashed purple and tinted glass. The flashed fill was then overpainted to match the original paint (*Figure 15*).

Cleaning was one of the most important steps in the conservation treatment. Clarke's painting technique involved much intricate detailing. Working with a needle, he removed pin pricks of paint through which light would sparkle by halation. Over time, as these filled-in with a film of dirt and, in some places, with an original over-application of putty, the window's glittering appearance was greatly retarded.

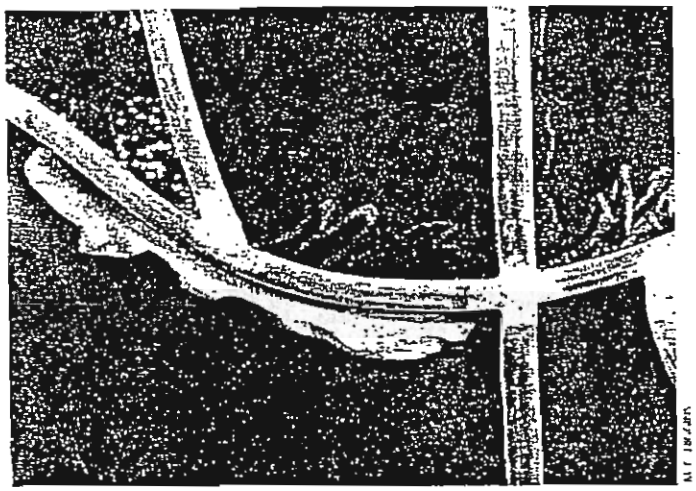
When the glass was removed from its leads for gluing, it became apparent that both the glass and the lead were quite strong and that opening up all of the leads from the back for cleaning would be possible without endangering the glass or damaging the leads. Large drips of original solder were found resting against the glass under the leads; these contributed to some of the breaks in the glass by holding it back in one corner while the rest of the glass could move slightly. These solder drips were removed.

There was quite a lot of dirt adhering to the glass paint on the front surface and trapped between the two layers of glass. When the window was first constructed a linseed oil putty was used to seal the leads. Over time, the putty broke down, allowing dirt and soot to filter in between the layers. A fine film of dirt settled on the two interior glass surfaces, and cut down on the amount of light passing through the glass. Because stained glass is totally reliant on transmitted light, any diminishment of this light will lessen the work of art. As the putty continued to dry out, particles of the putty fell and were trapped between the layers of glass.

All the glass was removed from its leads and cleaned. In this case, because the paint was in excellent condition, the glass was washed using 'Orvus,' a synthetic detergent of Sodium Lauryl Sulfate, then thoroughly rinsed with distilled water. Some additional cleaning was done using scalpels and fiberglass brushes. Once back in the leads, the glass panes were again resealed. All putty oils were completely cleaned off the glass.

When the glass was cleaned, small amounts of wax from the original etching process were found, as well as one instance in Panel #1 in which the medium from the silver stain application had never been removed (*Figure 16*). Since it is a very simple matter to wash off this medium, it was seen as an indication, supported by accounts of the panel's fabri-

Figure 16: 'The Wayfarer,' by Patrick Pearse. The silver stain medium left on the glass.



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cation, of the final rush to complete the ensemble. Analyzed in this light, the remaining medium was of historical interest and left in place on the glass.

The signature is partially covered by the leads. It reads: "Harry Clarke, Dublin 1930."

Conclusion

The sophistication and intricacy of Harry Clarke's stained glass art demand the utmost from the conservator. In order to do simple justice to the panel, the conservator must be conversant in a wide variety of fabrication and conservation techniques, yet must be able to meet the challenges presented with a minimum of ego. In the end, the spirit of the original work of art must be preserved and conveyed to a whole new generation of art lovers and scholars.

The Geneva Window was the last commission Harry Clarke saw completed, and it is certainly one of his masterpieces. The Irish government and powerful religious leaders had banned some of the authors and works represented, most of whom were well respected internationally. The authorities then rejected the visual interpretation of that work, a second act of censorship. Clarke certainly could have expected this, yet he nevertheless proceeded to challenge Ireland's official parochialism. *The Geneva Window* is the work of a mature artist, accomplished in his technique and sure of his vision. In pushing the limits of his craft, as well as the limits of his society's cultural mores, he left us an invaluable legacy and example in his window for the League of Nations. Ω

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THE SIGNIFICANCE OF THE REFRACTIVE INDEX OF ADHESIVES FOR GLASS REPAIR

Norman H. Tennent and Joyce H. Townsend

1 INTRODUCTION

The dual aim of the restoration of glass objects is to achieve a secure and aesthetically pleasing repair. In the past, it was often necessary to sacrifice appearance to the safety of the object by using metals, for example, to secure broken fragments [1], but now many synthetic resins are available which can bond broken fragments unobtrusively and replace missing parts [2-5]. A refinement of this approach is to attempt to achieve an 'invisible' repair by tailoring the optical properties of the adhesive to match those of the glass to be repaired.

The main factor which determines the appearance of a crack or gap in glass is the refractive index (RI) of the glass relative to the RI of the material filling the gap. Breaks or cracks in glass appear less obvious when joined by an adhesive than when held together with air in the gap. This is because the RI of air is a worse match for glass than the RI of adhesives. The more closely the RI of the adhesive matches the RI of the glass in question, the more the repair looks like unbroken glass. Adhesives have been described which attempt to match the RI of the glass [6,7] but these reports are restricted to glasses of a specific RI; a major practical problem for glass conservators is the wide range of RI likely to be encountered with historic glasses. The meaning of RI and its consequences for glass repair will be discussed in the following sections: a more theoretical treatment and some numerical results for different types of glass are presented in the Appendix. The significance of the RI of varnishes for paintings has been reported by Feller [8] and De Witte [9].

Once this investigation had begun it became clear that very few measurements of the RI for historic glasses had been reported, and then invariably as incidental measurements. Information on the RI of synthetic resins, from manufacturers or in the conservation literature, was also found to be scanty. The range of RI spanned by glasses and adhesives was therefore unclear and the possibility of tailoring the RI of adhesives to match a specific glass was unknown. In addition, methods for measuring the RI of glasses and adhesives were not well documented in the conservation literature. It was therefore necessary to survey suitable methods for determining RI and then to apply these methods to the measurement of a wide range of glasses and adhesives. Only then could the feasibility of achieving 'invisible' repairs by choosing an adhesive with a matching RI to that of any historic or artistic glass be assessed. Each of these topics is developed in this paper.

2 REFRACTIVE INDEX

2.1 *Description and relevance to glass repair*

The RI determines, or can be used to describe, the behaviour of light when it passes from one material to another of different composition. The discussion which follows applies to transparent glassy materials (including synthetic polymers) and materials which are glossy when polished (e.g. jade, gemstones and ceramic glazes). Metals are a different case altogether.

When light in a medium of low RI, such as air, meets a medium of higher RI, such as glass, a small proportion is reflected (because of the difference in RI) and about 96% is transmitted. The eye perceives and the brain interprets this fairly small difference as a different situation from empty air, and one sees the glass object. On the other hand, were the glass to be immersed in a liquid of matching refractive index, the glass would not be visible at all. (Many conservators are familiar with this phenomenon, for when Paraloid B72 spheres are added to toluene they 'vanish' because the RI of toluene (1.496) is a fairly good match to that of Paraloid B72 (1.487).)

The amount of light reflected varies with the angle of viewing (see Appendix). An air-filled break in the object provides two air/glass interfaces and since the fracture surface is generally irregular in profile, multiple reflections can result. Furthermore, the difference in RI between air and glass gives rise to a phenomenon known as the 'critical angle': at angles greater than the critical angle all the light is reflected back from that point in the glass and the visual impression is of a small area of polished, mirror-like metal (see Figure 1 for an example of this). Reducing the difference between the RI of glass and adhesive reduces the amount of light reflected, resulting in a more transparent appearance.

RI is measured at a specific wavelength, usually that of the sodium D line (589nm), and quoted values are often denoted by n_D.

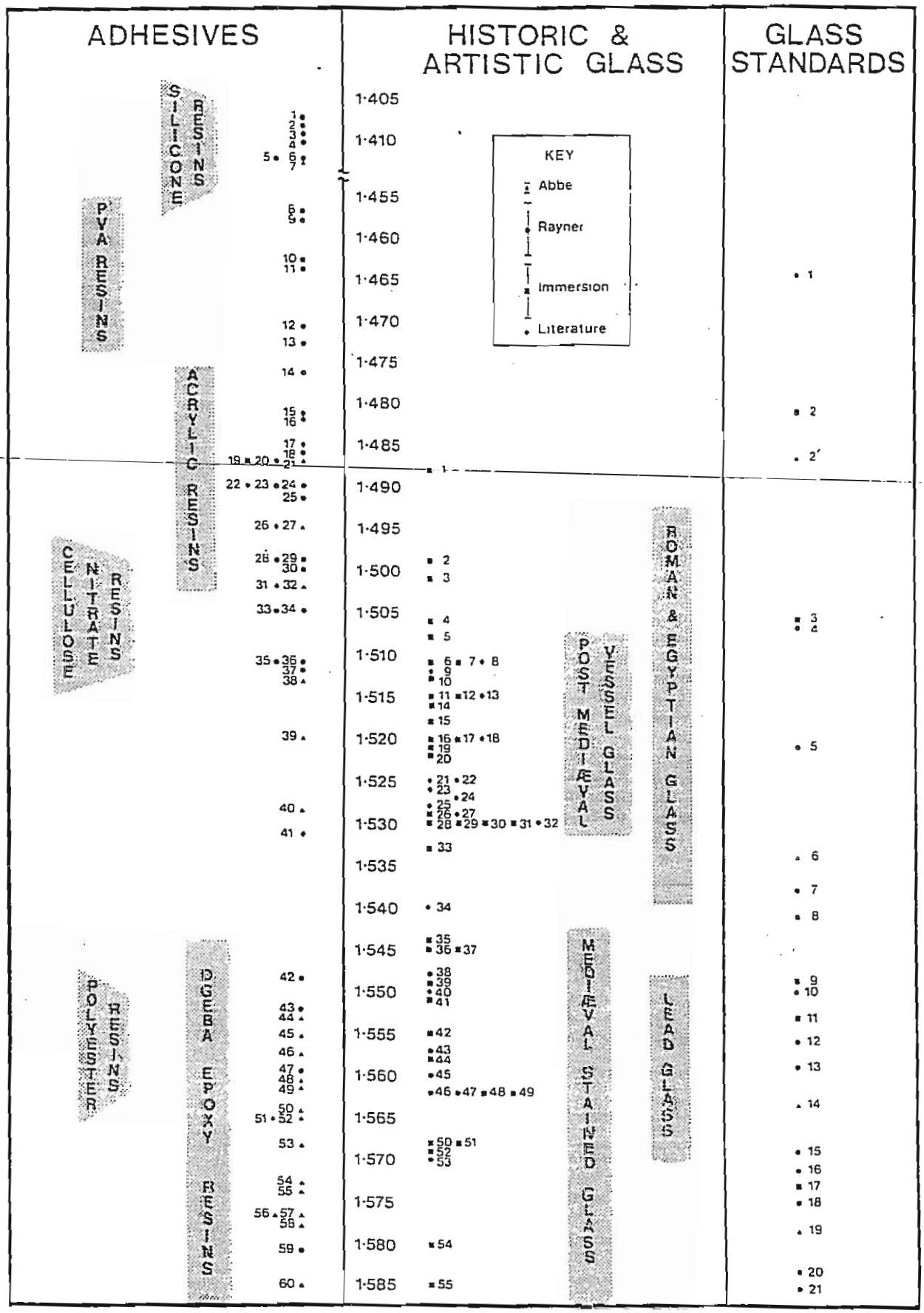
2.2 *Measurement*

Four techniques are available for measuring the RI of adhesives and glasses. The salient features of each method are summarized in Table 1.

Table 1 Techniques of RI measurement suitable for glass objects and adhesives

Technique	*Sample requirements*	*Accuracy*	*Comments*	*Example (Corning Glass Standard 'B')*
Rayner Refractometer, normal mode	Specimens with smooth flat surface ≥ 10mm x 4mm	± 0.003	Suitable for adhesives, stained glass and certain objects with flat areas	1.533 ± 0.003
Rayner Refractometer, distant vision	Curved specimens which allow minimal surface contact	± 0.01	Not the preferred method but suitable if other methods are not possible	1.53 ± 0.01
Abbé Refractometer	Specimens with polished flat surface ≥ 15mm x 15mm	± 0.0005	Cannot be used for most historic glasses, but the preferred method for adhesives	1.5342 ± 0.0005
Immersion	Specimens equivalent to the size of a grain of salt or less	± 0.003*	Suitable for broken glass or objects where sampling is possible. Also suitable for adhesives which do not dissolve in the immersion liquids	1.533 ± 0.003

* For immersion liquids spaced in units of 0.01


ADHESIVES
HISTORIC & ARTISTIC GLASS
GLASS STANDARDS
SILICONE RESINS
PVA RESINS
ACRYLIC RESINS
CELLULOSE NITRATE RESINS
POLYESTER RESINS
EPOXY RESINS
DGEBA
POST MEDIÆVAL VESSEL GLASS
ROMAN & EGYPTIAN GLASS
MEDIÆVAL STAINED GLASS
LEAD GLASS
KEY
Abbe
Rayner
Immersion
Literature
1·405
1·410
1·455
1·460
1·465
1·470
1·475
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1·585

Table 2

Key to Table 2

ADHESIVES

1	Arbosil Aquarium Sealant (*silicone*).	Adshead Ratcliffe & Co. Ltd, Belper, Derbyshire DE5 1WJ, UK.
2	Eccosil 2 CN (*silicone*).	Emerson & Cuming (UK) Ltd, 1 South Park Road, Scunthorpe, South Humberside DN17 2BY, UK.
3	Silastic 732 RTV (*silicone*)	Dow Corning Ltd, Reading Bridge House, Reading, Berks RG1 8PW, UK.
4	Dow Corning 3140 RTV (*silicone*)	
5	Dow Corning 3144 RTV (*silicone*)	
7	Sylgard 184 (*silicone*)	
6	Loctite Clear Silicone Sealant (*silicone*)	Loctite UK, Loctite Holdings Ltd, Watchmead, Welwyn Garden City, Herts AL7 1JB, UK.
30	Loctite 357 (*UV curing, urethane acrylic*)	
33	Loctite 350 (*UV curing acrylic*)	
38	Loctite 'Glass Bond' (*UV curing system*)	
8, 10	Rhodopas M (*PVA*): after casting from solution (8), as supplied (10)	Rhodia (UK) Ltd, 14 Essex St, London WC2R 3AA, UK.
9	Vinalac 5254 (*PVA*).	Vinyl Products Ltd, Mill Lane, Carshalton, Surrey, UK.
11	UHU 'All-purpose' (*PVA*).	Beecham UHU, Brentford, Middlesex, UK.
12	Evostik 'Resin W' (*PVA*)	Evode Ltd, Common Road, Stafford, UK.
35	Evostik 'Clear' (*cellulose nitrate*)	
13	Berol 'Merlin' (*PVA*).	Berol Ltd, Oldmedow Road, King's Lynn, Norfolk, UK.
14	Paraloid F10 (acrylic)	Rohm & Haas (UK) Ltd, Lennig House, 2 Mason's Avenue, Croydon CR9 3NB, UK.
15, 19	Paraloid B72 (acrylic): after casting from solution (15), as supplied (19)	
16	Paraloid B82 (*acrylic*)	
18	Paraloid B67 (*acrylic*)	
20	Paraloid B66 (*acrylic*)	
23	Paraloid A30 (*acrylic*)	
25	Paraloid B44 (*acrylic*)	
17	Butvar B76, B79 (*polyvinyl butyral, PVB*)	Monsanto Ltd, Monsanto House, 10-18 Victoria Street, London SW1 0NQ, UK. (Manufacturer's data)
22	Butvar B72, B74, B90, B98 (*PVB*)	
26	Formar 12/85 (*polyvinyl formal, PVF*)	
31	Formar 5/95E, 6/95E, 15/95E (*PVF*)	
21	Plastogen G (*acrylic*)	Frank W. Joel Ltd, Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk PE30 4HH, UK.
28	Durafix (*cellulose nitrate*)	
34	HMG (*cellulose nitrate*)	
36	Frigilene (*cellulose nitrate*)	
37	Ercalene (*cellulose nitrate*)	
40	Rutapox 1200 (*epoxy*)	
44	Plastogen EP (*epoxy*)	
57	Rutapox 1210 (*epoxy*)	
24	Lascaux Acryiglasur 40X (*acrylic*).	Alois K. Diethelm Farbenfabrik, CH-8306 Brüttisellen, Switzerland.
27	Technovit 4004A (*acrylic*).	Rubert & Co. Ltd, Dennings Road, Cheadle, Cheshire, UK.
29	Bostik 5293 adhesive (*cellulose nitrate*).	Bostik Ltd, Ulverscroft Road, Leicester LE4 6BW, UK.
32	L R White Resin (*acrylic*).	London Resin Co., PO Box 24, Basingstoke, Hants RG22 5AS, UK.
39	HXTAL NYL-1 (*epoxy*)	Conservation Materials Ltd, 340 Freeport Blvd, Sparks, NV 89431, USA.
50	Ablebond 342-1 (*epoxy*)	
51	Devcon '2-ton' (*epoxy*)	
52	Devcon '5-minute' (*epoxy*)	
41	Opticon UV-57 (*UV-curing system*).	Opticon Chemical, PO Box 2445, Palos Verdes Peninsula, CA 90274, USA [6].
42	Norland Optical Adhesive 63 (*UV-curing system*)	Leader House, 117-120 Snargate Street, Dover, Kent CT17 9DB, UK.
47	Norland Optical Adhesive 61 (*UV-curing system*)	
59	Vitralit DAC (*UV-curing system*)	
43	Tiranti Embedding Resin (*polyester*).	A. Tiranti Ltd, 20 Goodge Place, London W1, UK.
45	Epotek 301 (*epoxy*).	Epoxy Technology Inc., 65 Grove Street, Watertown, MA 02172, USA.
46, 48	Metset Resin SW (*polyester*): first batch (46), second batch (48).	Metallurgical Services Laboratories Ltd, Reliant Works, Brockham, Betchworth, Surrey RH3 7HW, UK.
49	Araldite MY790/X83-19/DY040 (*epoxy*)	Ciba-Geigy Plastics and Additives Co., Plastics Division, Duxford, Cambridge CB2 4QA, UK.
55, 58	Araldite AY103/HY951 (*epoxy*): first batch (55), second batch (58)	
60	Araldite AY105/HY951 (*epoxy*)	
53	Epofix (*epoxy*).	Struers, Copenhagen, Denmark.
54	CXL (*epoxy*).	Resin Coatings Ltd, Colebrand House, 20 Warwick Street, Regent Street, London W1R 6BE, UK.
56	Permabond E27 (*epoxy*).	Permabond Adhesives Ltd, Woodside Road, Eastleigh, Hants SO5 4EX, UK.

HISTORIC & ARTISTIC GLASS*

1	GMAG/DA/96.38a. *Cristallo* (greenish) Venetian Tazza, 16th century.
2, 3	NHT. Clear (2) and violet (3) glass from Alexandrine *Zwischengoldglas* fragment, 1st century AD.
4	GMAG/BC/17.64. Dark blue transparent glass from Roman bottle, early centuries AD.
5	R/NM10754.248. Bohemian glass, wheel engraved, mid-18th century.
6, 28	GMAG/DA/97.50bv. Spanish (Catalonia) jug, clear glass, 18th century: vessel glass (6), ornament glass (28).
7	NHT. Clear glass from Islamic lamp fragment, 13th/14th century AD.
8	Egyptian vessel stamp, 8th century AD [19, Table 1].
9	Eleven Egyptian vessel stamps, coin weights, etc., 8th century AD [19, Table 1].
10	NHT. Clear glass from Islamic lamp fragment, 13th/14th century AD.
11	R/NM10754.270. Russian (?) covered beaker, wheel engraved, mid-18th century.
12	GMAG/A/03.185gp. Cypriot glass flask, early centuries AD.
13	Egyptian beads: one pale green from Tell Asmar, 2700-2500 BC [15, p.10, specimen no.7]; two blue from Qau, 7525 [16].
14, 16	NHT. Transparent amber (14) and blue (16) glass from Alexandrine lozenge-shaped decorative glass, *c.* 1st century AD.
15	R/NM8326. Bohemian glass, wheel engraved, 1725-1750 AD.
17	GMAG/A/03.185iz. Cypriot glass dish, early centuries AD.
18	Egyptian blue bead from Tell el-Amarna, XVIII Dynasty [16].

* Explanation of registration codes: GMAG/DA, GMAG/BC, GMAG/A = Glasgow Museums and Art Galleries, Department of Decorative Art, Burrell Collection, Department of Archaeology, respectively; NHT = author's collection; R = Rijksmuseum, Amsterdam.

19 GMAG/DA/97.50cq. Southern Spanish bull-shaped ornament, green glass. 19th century?

20 GMAG/DA/97.50bu. Spanish (Catalonia) jug, clear glass. 16th century?

21 Three Egyptian red beads from Armant, 1200A [16]. XII Dynasty.

22 Egyptian vessel stamp, early-middle 8th century AD [19, Table 1].

23 Egyptian ring weight, 8th century AD? [19, Table 1].

24 Egyptian green glass bead from Qau, 612 [15, p.14, specimen no.1]. XI Dynasty [16].

25 Egyptian coin weight, early 9th century AD [19, Table 1].

26 GMAG/DA/96.38c. Venetian wine glass, late 16th century.

27 Egyptian coin weight, late 8th/early 9th century AD [19 Table 1].

29, 54 GMAG/DA/93.93w. Blue (29) and opal (54) glass from Venetian wine glass. 16th/17th century.

30 NHT. Transparent dark blue vessel glass fragment. Tell el-Amarna. XVIII Dynasty.

31 GMAG/BC/17.49. Pale green glass from Roman jar, early centuries AD.

32 Arabic bead from Assint, probably 14th-18th century AD [16].

33 NHT. Transparent turquoise vessel glass fragment. Tell el-Amarna. XVIII Dynasty.

34 Transparent pink bead from Armant, 1200A [16].

35, 36, 37, 55 Excavated mediaeval stained glass from St Andrews Cathedral (35: StA1) and Elgin Cathedral (36: EC4, 37: EC5, 55: EC1). See [17] for analytical data.

38 GMAG/BC/45.470. Clear glass from Flemish roundel, early 16th century.

39 GMAG/DA/97.50bo. Spanish (Andalusia) vase, green glass, 17th century.

40 Clear dark blue bead from Armant, 1213D [16].

41 GMAG/DA/27.90e.3. Water-glass. Scottish (John Baird Glassworks), c. 1881.

42 GMAG/BC/45.484. Clear, blue and green glass from German (Nuremburg) stained glass panel, c. 1470-1480.

43 GMAG/BC/45.462. Clear glass from Flemish roundel, 16th century.

44, 49 GMAG/DA/88.65a. Clear (44) and yellow (49) glass from ruby glass goblet. Rhine Glass Works Co., c. 1888.

45 GMAG/BC/45.17. Clear glass border dated 1577 (enclosing a 14th century roundel).

46 GMAG/BC/45.551. Clear glass from Dutch panel, dated 1686.

47 GMAG/BC/45.499. Clear glass from Swiss panel, late 16th century.

48 GMAG/BC/Inv 151. Wine glass. Dutch/British, mid-18th century.

50 R/NM10754.78. Wine glass, stipple engraved. Dutch, late-18th century.

51 R/NM4015. Wine glass, diamond engraved. English, 1725-1750.

52 R/RBK 1966.61. Wine glass, wheel engraved in Holland. English, c. 1750.

53 GMAG/45.32. Clear glass from English panel, 14th century.

GLASS STANDARDS

1	Glass FK3: Schott Glaswerke, Hattenbergstrasse 10, D-6500 Mainz, W. Germany.	
2,2'	Glass Standard No 4	Society of Glass Technology, 20 Hallam Gate Road, Sheffield S10 5BT, UK.
3	Glass Standard No 5	
11	Glass Standard No 3	
4	Zinc Crown, ZC 508612	Pilkington Brothers plc, Research & Development Laboratories, Ormskirk, Lancashire L40 5UF, UK.
5	Hard Crown, HC 524592	
7	Extra Light Flint, ELF 541472	
8	Extra Light Flint, ELF 548456	
15	Light Flint, LF 567428	
19	Light Flint, LF 579411	
6	Glass Standard B	Standards prepared for the Corning Museum to simulate the composition of ancient glasses [21].
9	Glass Standard D	
10	Standard 76-C-151	Series of synthetic mediaeval stained glass compositions prepared by Pilkington Brothers for Professor R.G. Newton [22].
12	Standard 76-C-158	
13	Standard 76-C-149	
14	Standard 76-C-144	
16	Standard 76-C-150	
17	Standard 77-C-33	
18	Standard 76-C-145	
20	Standard 76-C-147	
21	Standard 76-C-148	

A description of the Abbé refractometer and its mode of operation is available in standard optics textbooks [10]. The authors have found the Rayner refractometer to be an attractive, cheaper, simpler and more versatile alternative, though not capable of the accuracy of the Abbé. RI measurements made to ±0.003 are, however, of more than adequate accuracy for the selection of matching adhesives for glass repair. The immersion technique is widely used for mineralogical studies and is also well described in many textbooks [11,Ch.3; 12,Ch.3]. It is based on the observation of a tiny sample through the microscope (40-50x magnification): a series of liquids of known RI is used to immerse the sample until a liquid is found in which the sample disappears. The selection of the relevant immersion liquid is facilitated by observing the behaviour of the Becke line [11,12]. Immersion liquids are available commercially in steps of 0.005 or 0.01. Alternatively, a graded series of liquids of varying RI can be prepared by mixing two terminal liquids [13,14]. The properties which these liquids should possess are well documented [14]; mixtures of butyldigol (RI 1.431-1.433) and 1-chloronaphthalene (RI 1.632-1.634) are suitable for the work described in this paper.

Adhesives were examined primarily with the Abbé refractometer or, for less accuracy but greater convenience (since sample quality is of less importance), the Rayner refractometer. A sodium lamp, or a suitably filtered light source, was used. The adhesives were either cast and polished or prepared as a thin film either on a glass microscope slide or directly on the prism of the refractometer. In the former instances the contact liquid, 1-chloronaphthalene, may dissolve some resins. In certain cases the resin was examined by immersion, but this method was found to be more useful for glasses where a tiny fragment can be removed from a broken piece. Even for intact glass objects, sufficient sample can usually be removed unobtrusively by means of a diamond-tipped probe.

3 RESULTS

3.1 *The refractive indices of adhesives and glasses*

The results of RI measurements on a variety of adhesives, historic glasses and glass standards are presented in Table 2. Specific results are plotted individually and may be identified by means of the key to the Table. Examination of these measurements shows up certain groupings of adhesives and glasses, and these are indicated in the Table by the shaded areas, the terminal points of which are somewhat uncertain.

It is clear from the Table that historic and artistic glasses span a wide range of RI, principally from *c.* 1.480-1.580, which indicates the problems of tailoring the RI of an adhesive to match closely that of a glass requiring restoration. Fortuitously the span of glass RIs is well matched by that of different classes of synthetic polymers: for example, most amine-cured epoxy resins examined fall in the useful RI range 1.550-1.585, but silicone resins span the range 1.405-1.415, and are therefore unsuitable for giving a close RI match for glass repair. (It is an interesting and useful offshoot of this work that polymer classes and glass types can often be identified on the basis of their RI. This is not surprising, since the RI is a consequence of composition, though in the case of glasses, density is a more suitable probe for characterization purposes. Weathering and the annealing process can both affect the RI of glasses [18,19].)

The grouping of historic glasses includes some literature values. Although few measurements of RI for historic glasses have been published, data are available on several dozen glass artifacts and experimentally-melted counterparts of similar compositions, which will be published in due course [20]. The values for historic glasses in Table 2 are mirrored by those for specially prepared glass standards, designed to simulate the compositions of early glasses [21,22].

The RIs of several adhesives and glasses were determined by more than one method. Agreement was within experimental error (see, for example, Table 1).

It has been found that the RI of adhesives changes during cure or drying, so during the restoration of glass the initial appearance of the repair will be modified. The values given in Table 2 are for fully cured resins or solvent-borne resins after several days' drying. Adhesives from the latter group may never regain the RI of the resin prior to the addition of solvent. The RI of Rhodopas M PVA resin, for example, was 1.451 ± 0.003 immediately after preparation, 1.455 after several days and 1.457 after several years. The RI of the resin as supplied was 1.463. This illustrates the plasticizing effect of the solvent, which was still noticeable in the oldest sample.

Although the proportions of hardener and resin can affect the RI (see section 3.3), good consistency (variations of ± 0.001) was shown by several Ablebond 342-1 epoxy resin samples prepared with the same proportion of resin to hardener. Different batches of Metset SW polyester resin showed equally high consistency in RI.

The dispersion (a slight variation of RI with wavelength throughout the visible spectrum) of glasses and adhesives has not been studied. It can be assumed that this, and the very small temperature dependence of the RI, will be swamped by other causes, namely batch-to-batch variation in adhesives and variations due to working the glass surface during the manufacture of the object.

3.2 *The effect of matching the refractive index of adhesives and glass*

Figure 1 illustrates the significance of RI in the repair of a cracked lead glass vessel (RI 1.558 ± 0.003) by means of clear, low viscosity resins. For this repair, two different water-white epoxy resins were used to fill the crack which runs from the rim of the vessel to its base.

Ablebond 342-1 was selected from Table 2 as an adhesive whose refractive index, 1.5646 ± 0.0005, matches very closely the glass in question. The resin was applied carefully along the upper half of the crack and was drawn in by capillary action. As the resin penetrated, the crack immediately became less visible. The excess resin was wiped away from the surface of the glass and the vessel set aside for two days at room temperature to allow the resin to cure fully. By this time only a very faint hairline could be seen to indicate the position of the break. (A chip half way along this section of the crack was not filled and remained quite visible (Fig. 1b).)

HXTAL NYL-1, an epoxy resin of equal water-white clarity to Ablebond 342-1 but whose RI, 1.5201 ± 0.0010, differed from the glass by 0.038, was used to fill the remainder of the crack down to the base of the vessel. The same procedure was adopted, but since this resin cures very

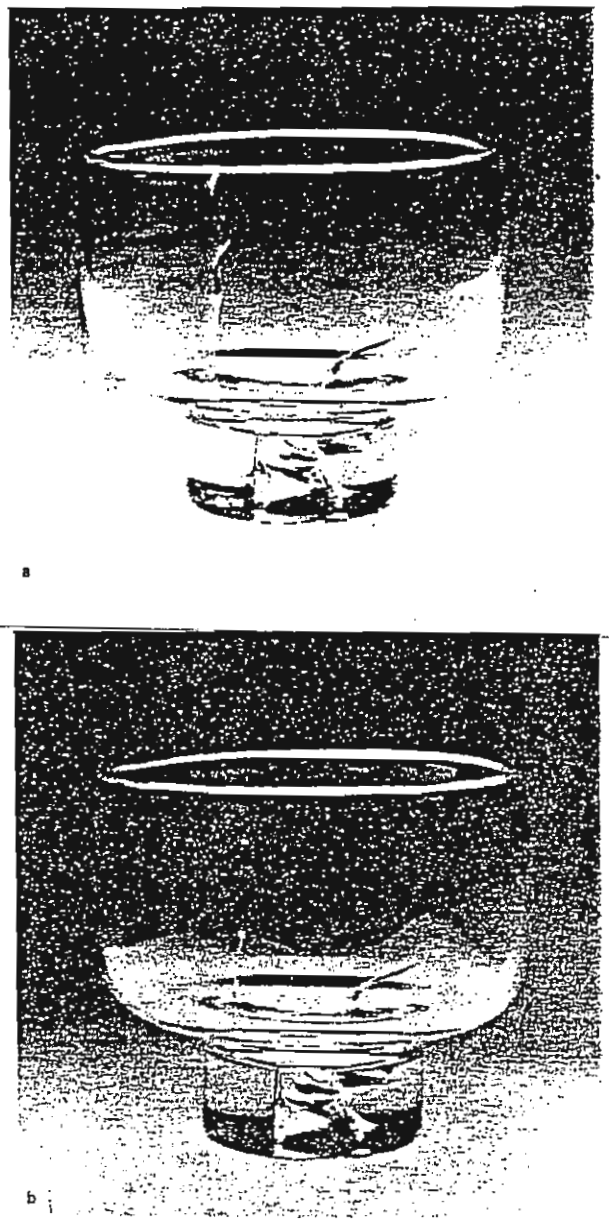

Fig. 1 Modern lead glass bowl (RI 1.558) before (a) and after (b) repair with Ablebond 342-1 epoxy (RI 1.565) above the arrow and HXTAL NYL-1 epoxy (RI 1.520) below it.

slowly at room temperature, seven days elapsed before cure was complete. For this resin the crack also appeared less visible than before restoration, especially at certain angles of viewing. At other angles, however, total internal reflection of light occurred (see section 2.1) and the crack appeared as a silvery line (Fig. 1b). This was not the case with the part of the crack mended with Ablebond 342-1.

It is clear, therefore, that for resins chosen to match as closely as possible the RI of broken or cracked glass, the quality of the repair is superior to cases where a mismatch of even 0.04 occurs.

3.3 *Modification of the refractive index of commercial adhesives*

While the range of commercial adhesives given in Table 2 is a good starting point for the selection of an adhesive which matches the RI of any given glass object, there remain instances where this tabulation might not permit a suitable adhesive to be chosen. The Table can be extended in two ways: by the addition of new commercial products or by the ability of conservators to modify marginally the RI of a particular commercial product.

Since epoxy resins represent the most useful class of adhesive for glass bonding the investigation has been restricted to these resins. Three approaches have been explored: the effect of using different hardeners for a single epoxy resin component, the effect of marginally changing the proportion of hardener and the effect of the addition of other components, principally plasticizers and diluents. (The addition of dyestuffs does not affect the RI of a resin.) These results are reported in full elsewhere [23] but it is relevant to summarize the conclusions here.

It is possible to cure successfully a series of commercial resins based on the diglycidyl ether of bisphenol A (DGEBA) with amine hardeners other than those specified by the manufacturer. This is to be expected, since the DGEBA resin components of these epoxies are generally similar. RI variations in the range 0.011 to 0.026 were found when a set of epoxy resins was cured with alternative hardeners [23].

A factor which may play some part in these RI modifications is the ratio of hardener to resin. This factor was investigated separately and it was found that RI changes of the order of 0.003 can be produced by a variation in hardener proportion of 25% from the recommended value [23].

The addition of dibutyl phthalate was also found to affect the RI of the cured epoxy resin [23]. In fact, the presence of dibutyl phthalate is the main reason for the difference in the RI of Araldite AY103/HY951 and AY105/HY951 (Table 2).

Tampering with resin formulations in these ways creates the risk that the properties of the cured resin will be adversely affected. It has been observed, for example, that light-induced yellowing of certain resins is more pronounced when alternative hardeners are used but in other cases an improvement in light stability actually results [23]. The effect on adhesive strength has not been examined.

For crack mending, however, the tendency of a resin to yellow is of less importance than the ability of the RI to match the glass undergoing repair. A simple experiment served to prove this point: a crack in a lead glass vessel (RI 1.558) filled with a solvent of matching RI (nitrobenzene, 1.553) dyed an intense yellow colour was less visible than the same crack filled with a water-white liquid of differing RI (toluene, 1.496). It is implicit in this argument that the yellowing process does not greatly affect the RI of the resin. This has been found to be the case [23]. For restored breaks where the resin has a significant thickness, on the other hand, the yellowing of the resin can become obtrusive.

3.4 *Synthesis of adhesives with a specified refractive index*

An alternative approach, not pursued in the course of this work, is the synthesis of adhesives with predetermined RIs. This is in principle quite possible but is unlikely to become a practicable reality for most conservators. De Witte adopted this course of action [9] in order to prepare acrylic picture varnishes with a high RI. It is also relevant that copolymerization of isobutyl methacrylate and styrene in

prescribed proportions has been reported to give a graded set of mounting media for microscopical sections in the range 1.477 to 1.590 [24].

4 PRACTICAL FACTORS IN ACHIEVING A HIGH QUALITY REPAIR

In this study most visual assessments of the significance of RI in glass repair were made on cracked glass because this avoided the need to align broken fragments, but for both cracked and broken glass certain steps can be taken to ensure an optimum appearance.

4.1 *Cracked glass*

1 The adhesive strength required for bonding cracks is less than that for bonding broken fragments, so the range of suitable polymers can be extended to include classes such as acrylics which are not good adhesives for glass. It is also possible to use adhesives whose resistance to yellowing is not of the first order for very narrow cracks (see section 3.3).

2 Since there is evidence that the RI of an old crack may differ by as much as 0.235 from that of the bulk glass [25] it is advisable to refine the RI measurement, made initially by one of the methods described in section 2.2, by determining which of a series of immersion liquids drawn in by capillary action makes the crack least visible.

3 Once an adhesive of appropriate RI has been selected, a greater speed of penetration of the crack by capillary action can be achieved by warming the resin to reduce its viscosity. (For a discussion of the relevant factors involved in enhancing penetration during consolidation see [26.Ch.7].) The danger of the crack spreading if the glass itself is heated should be borne in mind.

4.2 *Broken glass*

1 Alignment of the broken fragments is all-important. Sometimes taped pieces move slightly during cure or drying of an adhesive. A valuable technique is the application of an initial small, securing spot of cyanoacrylate adhesive prior to bonding by the chosen adhesive [27]. Cyanoacrylate adhesives are not recommended as the sole adhesive for glass bonding as in time the bond will fail.

2 When bonding fragments of flat glass such as stained glass (or even gently curved pieces) it is helpful to ensure that the best fit is achieved, with the fragments lying in the correct plane, by observing the reflection of a fluorescent lighting tube in the glass. If this appears smooth and unbroken then the glass is positioned correctly.

4.3 *Cracked or broken glass*

The hairline crack which remains on the glass surface after bonding is caused by the resin creating an imperfectly smooth surface with the glass. This can be minimized by smoothing out a tiny excess of resin along the edge of the crack or break with a 12μ-thick Melinex (polyethylene terephthalate) film. This can be peeled away when the resin has set. (One disadvantage of HXTAL NYL-1 epoxy resin is that it bonds so firmly to Melinex that this technique cannot be used.)

5 CONCLUSIONS

Several issues have been clarified as a result of this investigation. The range of RI spanned by adhesives and the RI values typical of historic and artistic glasses have been identified. In the course of these measurements the most suitable methods for the determination of such RIs have been ascertained. These results have been used to show that it is possible to achieve a good match between the RI of adhesives and most glasses. Experiments in the repair of glass have demonstrated that tailoring of the RI of an adhesive to that of a broken or cracked glass does enhance the quality of the repair. When a very close (± 0.003) match is achieved, invisible repairs almost become a possibility, though the ethical justification for this degree of perfection remains open to question. For most practical purposes it has been shown that a match of *c.* 0.01 can lead to an almost invisible repair, and that a mismatch of *c.* 0.04 can leave the break or crack readily visible. These findings are of most relevance to those glasses, especially post-mediaeval vessel glass, where the glass surface is not badly weathered.

It is a valuable additional conclusion of this study that RI determination provides a good means of differentiating certain polymer classes and glass types.

ACKNOWLEDGEMENTS

Many people have been of assistance at various stages in this investigation. The authors would like to record their thanks to Mr A. Hodgkinson, Jewellery Consultant, for the loan of a Rayner Refractometer and for helpful discussions on RI measurement, to Mr B. Jackson (Royal Scottish Museum) for access to immersion liquids and to Dr W.J. Rodger (Strathclyde Police Forensic Science Laboratory) for the use of an Abbé Refractometer. Professor R.G. Newton supplied the synthetic mediaeval stained glasses and Dr R. Brill provided the Corning Glass Standards and many helpful comments at an early stage in the project. Thanks are also due to Miss H. Adamson, Mr B.J.R. Blench and Dr R. Marks for permission to study glass from the Departments of Archaeology, Decorative Art and the Burrell Collection, Glasgow Museums and Art Galleries, and to Dr P. Ritsema van Eck who encouraged examination of the Rijksmuseum glass. Experimental glass was supplied by Strathearn Glass, Pilkington Brothers Ltd and Schott (UK) Ltd. The assistance of Mrs Haggit Meyer in the preparation of certain polymer samples is also gratefully acknowledged. The award of a Research Fund Grant from the Royal Society of Chemistry enabled purchase of a Rayner Refractometer and a series of immersion liquids.

SUPPLIERS OF EQUIPMENT AND MATERIALS

Rayner Dialdex Refractometer; sets of immersion liquids: Gemmological Instruments Ltd, St Dunstan's House, Carey Lane, London EC2V 8AB, UK.
Butyldigol: 1-chloronaphthalene: MacFarlane Robson Ltd, Burnfield Avenue, Glasgow G46 7TP, UK.
Melinex: Frank W. Joel Ltd, Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk PE30 4HH, UK.

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APPENDIX

The refractive index (n_2) of a medium is given by the ratio of the velocity of light in vacuum to the velocity of light in the medium. For numerical purposes, n (air) = 1, as for a vacuum. The velocity of light in any medium is less than in vacuum, so in consequence light which enters a medium of higher RI at an angle of incidence θ_1 is refracted at a smaller angle θ_2, as shown in Figure 2. For a medium of lower RI (n_1).

$$n_2/n_1 = \sin\theta_1/\sin\theta_2.$$

When light is travelling from glass to air and θ_1 reaches 90°, θ_2 is called the critical angle θ_c, and all light leaving the glass surface at θ_c or a higher angle is reflected back. This is known as total internal reflection. The critical angle is given by

$$\sin\theta_c = n_1/n_2.$$

Classical electromagnetic theory (Maxwell's equations) applied to a flat, non-magnetic air-medium boundary such as glass, leads to the result that light at normal incidence is partially reflected. The proportion reflected is given by

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)}$$

A refinement of the theory to angles of incidence other than the normal introduces polarized light (Fresnel reflection). Since the eye cannot detect polarization, the results for the two polarized components have to be summed to indicate what one would see at each viewing angle. Graphs of calculated values [28,p.400] indicate that the simpler equation given above is valid for viewing angles of 40° for soda glass in air. Some values for typical glasses are given below, in Table 3. A justification for these results is available in standard physics texts (e.g. [29]).

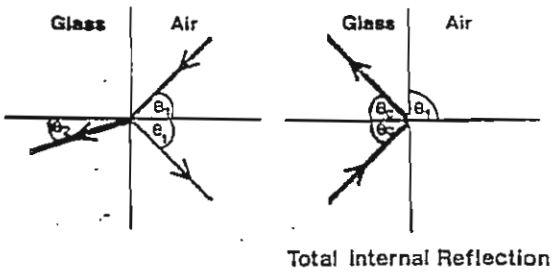

Fig. 2 Behaviour of light at an air-glass boundary.

Table 3 Calculated values of the critical angle and the percentage of light reflected, for various glasses in different media

Glass in medium of lower RI	n_2	n_1	θ_c	*R*	*Viewing angle for which R is valid*
Early glass in air	1.45	1.00	44°	3.4%	40°*
Soda glass in air	1.52	1.00	41°	4.3%	36°*
Soda glass in matching adhesive	1.52	1.51	83°	0.00001%	+
Lead glass in air	1.58	1.00	39°	5.1%	33°*
Lead glass in matching adhesive	1.58	1.57	84°	0.00001%	+

* From [28,p.401].
\+ R = 0.1% at 80°, 6% at 85°, and much less at lower angles.

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"Crizzling - A Problem in Glass Conservation"

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1. INTRODUCTION

Crizzled glasses are familiar to all curators or collectors who have handled much early English or European glass, the word 'crizzled' being used to describe the appearance of certain glasses which have a diminished transparency owing to very fine surface crazing. A typical example is illustrated in Figure 1. Under the microscope, a network of fissures can be seen clearly on the surfaces of such glasses, as shown in Figure 2. On those glasses which are most severely afflicted, small bits of glass may have spalled away. The effect is the result of unstable chemical compositions which render the glasses susceptible to chemical attack by water, usually in the form of water adsorbed from the atmosphere.

Crizzling is most often associated with glasses made in the seventeenth and eighteenth centuries, but earlier examples may exist, and nineteenth century examples are by no means rare. The glasses come from rather widespread areas encompassing England, Western Europe (including Venice), Scandinavia, North America, and China. There are numerous pieces, which are known to have been crizzled for a long time, throughout all of the large collections dealing with glass of this period.

Crizzling is one variant of what has often been called 'sick glass' — a persistent, but not very precise term referring to various forms of surface deterioration. These range from a slightly cloudy or dulled appearance, to crizzling, to occasional occurrences of 'weeping glasses' or 'sweating glasses', which repeatedly generate slippery surface films or droplets if exposed to humid conditions. All are related in that they are manifestations of hydrolytic attack by atmospheric water, but we will be concerned here primarily with the crizzling phenomenon.

Perhaps the best known crizzled glasses are those made by George Ravenscroft, the English glassmaker credited with being the first to capitalize on the properties of lead glasses. During his early experimentation, Ravenscroft made some pieces which crizzled within a few months of manufacture, a deficiency which he quickly attempted to correct [1].

Several treatments have been suggested for crizzled glasses. Most of these involve impregnations with polymeric materials which consolidate the surface and restore transparency and a glassy reflectance. The first application of this type of treatment known to the author was that by Professor J. Arvid Hedvall of Uppsala University [2]. Actually, however, none of the treatments we have seen have yielded entirely satisfactory results. Because storage under proper conditions and careful handling seem to forestall further damage to already crizzled glasses, the outlook of The Corning Museum has been to postpone treatment until a completely safe and satisfactory treatment has been perfected. This is still bur outlook as far as already crizzled glasses are concerned, since these objects seem to be stable for the present.

However, it has recently become known that there is a related and most urgent problem concerning crizzling [3]. There exists a category of glasses in early stages of crizzling, which have taken up water over the centuries but which do not exhibit very obvious signs of deterioration. Only when they are handled and turned around under correct lighting conditions can the telltale silvery rays of beginning crizzling be seen. These glasses are of the same general origins and dates as the already crizzled glasses. They have become hydrated and 'equilibrated' over the centuries with humid environments. When brought into centrally-heated galleries or apartments, they may be subjected abruptly to very dry conditions during the winter months. For example, in our galleries the relative humidity frequently drops into the 20 — 30% range during midwinter, and upon occasions has even fallen below 15% on extremely cold days. Under such conditions these hydrated glasses become dehydrated, and the crizzling fissures, which were not very evident to begin with, open up and propagate a network of hairline cracks across the surface. Thus, these glasses can become severely crizzled — and this may happen in the course of only a few months. We have observed one serious example of this effect in our museum and suspect that a half-dozen or so other objects have deteriorated to a less marked degree over the years. In addition, we have heard several reports of similar occurrences throughout North America, Europe, and Britain.

While most of the occurrences of this accelerating deterioration which have come to our attention involve vessel glasses, the author has examined one roundel of fifteenth century German glass (a glass bearing painting and silver-stained regions) which has developed an effect akin to crizzling over the past decade or so. Since it had hung adjacent to a heating register during that period, it seems very likely that a dehydration process was the cause of its accelerated deterioration.

By way of definition we have coined the term 'incipient crizzling', to describe this dangerous metastable state of deterioration. It designates glasses which are hydrated and in the initial stages of crizzling (the damage being apparent only under careful inspection) and which are susceptible to a rapid surface deterioration should they be exposed to dehydrating conditions. The object of the research which follows was to arrive at recommendations for the safe storage of glasses with incipient crizzling so as to prevent their disintegration into a severely crizzled state. We are less concerned for the moment with already crizzled or 'weeping' glasses.

Based mainly upon intuition and a few preliminary observations, we recommended earlier that glasses which show incipient crizzling should not be exposed to low relative humidities, that the temperature and humidity should be maintained at relatively constant levels, and that localized high temperatures, such as could result from installations with dramatic lighting, should be strictly avoided. Since then, some further progress has been made towards making firm suggestions as to safe exhibition and storage conditions based upon actual laboratory studies. The general approach to this research has been:

1. To obtain fundamental chemical information on susceptible glasses.

Table 1. Analyses of some crizzled glasses

		Venetian(?) c. 1709 colourless 457	Venetian(?) c. 1709 colourless 461	French c. 1750 colourless 449	French 1600-50 grayish 1050	French 1725-50 colourless 1498	Silesian* 1710-30 colourless 4011	American 1790-1810 colourless 1487	American 19th C. colourless 1488	American late 19th C. light blue 1630	Jamestown* 1971 green 1823
SiO_2	d/g	≈ 76	≈ 67	76.0	70.7	≈ 74	≈ 73.5	≈ 69	≈ 77	≈ 81	≈ 67
Na_2O	a	0.13	0.99	0.89	17.7	0.29	0.39	2.62	5.00	12.7	17.5
CaO	a	1.30	0.30	0.22	1.53	2.87	1.61	3.19	2.72	1.96	4.66
K_2O	a	18.7	18.4	18.7	3.42	19.9	16.6	24.2	12.7	2.24	6.82
MgO	a/s	0.04	0.06	≈ 0.1	≈ 0.1	0.22	0.03	0.20	0.32	0.12	0.10
Al_2O_3	a/s	≈ 0.1	≈ 0.05	≈ 0.5	≈ 0.5	1.95	1.03	0.55	1.51	0.44	2.61
Fe_2O_3	a/s	≈ 0.05	≈ 0.1	≈ 0.05	≈ 0.1	0.03	0.002	0.05	0.01	0.03	0.28
MnO	a/s	≈ 0.01	≈ 0.05	0.45	0.38	0.51	0.04	< 0.01	0.00X	0.00X	0.01
PbO	q/s	2.22	12.8	0.002	0.01	nf	5.88	< 0.01	nf	1.5	0.05
As_2O_5	q	1.66	0.24	---	-	---	..	.	≈ 0.5	≈ 0.2	

Notes:

*All glasses except 1823 and 4011 are heavily crizzled. 1823 is hygroscopic but uncrizzled; 4011 shows incipient crizzling.

Analyses by R. H. Bell and C. A. Jedlicka of Lucius Pitkin, Inc., NYC, and P. B. Adams of Corning Glass Works.

a – atomic absorption.
q – quantitative, various methods.
s – emission spectrography.
g – gravimetry.
d – SiO_2 by difference.
≈ – denotes spectrography.
nf – sought but not found.

Also found in varying trace levels: TiO_2, CuO, CoO, Ag_2O, BaO, SrO, Li_2O, Rb_2O, B_2O_3, ZrO_2. P_2O_5 contents uncertain but generally less than 1.0%. Where no As_2O_5 given, values are uncertain but less than 1.0%.

2. To characterize the crizzling process physically and chemically.
3. To evaluate the chemical durability of the susceptible glasses relative to other types of glass.
4. To duplicate crizzling in the laboratory on both synthetic glasses and actual pieces of early glass.
5. To identify the primary factors controlling the chemical mechanism of crizzling. (Although it would be desirable to establish the details of the mechanism in the sense of a true reaction and kinetic study, this is not feasible just now.)
6. To arrive at recommendations as to how to prevent susceptible glasses, those showing incipient crizzling, from deteriorating into severe crizzling.

2. CHEMICAL COMPOSITIONS OF CRIZZLED GLASSES

It has generally been held that crizzling is caused by the attack of atmospheric water, possibly augmented by the uptake of carbon dioxide, and that the susceptibility of the glasses to hydrolysis is the result of a deficiency in lime, the most common stabilizer in glasses. While we also held that view — and still do — it seemed worthwhile to confirm it by chemical analyses. Therefore, chemical analyses were made of several early crizzled glasses, eight of which are reported in Table 1. To simplify the table, only major and minor constituents are reported. Data on trace elements have been excluded. Also included in the table are an example of a glass showing incipient crizzling (no. 4011) and one of a modern glass (no. 1823). Both of the latter were used in experiments aimed at duplicating crizzling in the laboratory. (Descriptions of the glasses analysed are given in the Appendix.).

For working within the system $Na_2O:CaO:SiO_2$ (soda-lime-silica glasses), a lime content of less than about 4% by weight would be regarded as very unstable by present-day standards. Even among ancient glasses, lime contents are ordinarily greater than 5.5—6.0%, and many of them are heavily weathered. It will be seen, however, that only two of the early glasses in Table 1 (nos. 1050 and 1630) are actually soda-lime glasses. The others are in the $K_2O:CaO:SiO_2$ system (potash-lime-silica glasses) or are glasses containing some lead (PbO). The minimum concentration of lime required to stabilize a potash glass may not be just the same as the 4% level cited above for the soda-lime glasses, but it is certainly not very different from that level.

It is quite apparent from the table that all of these glasses are indeed seriously deficient in lime and should be expected to be prone to hydrolysis. Only nos. 1487 and 1823 might be judged to have borderline lime contents and these both have such excessively high total alkali contents that they would also be expected to be very unstable. (A total alkali content of 20% or greater would not be tolerated by modern commercial standards, and ancient glasses with that much alkali are usually very heavily weathered.) Nos. 461 and 4011 are the only glasses of this group which really qualify as lead glasses, and while we have not yet completed our literature search on durabilities within the system $K_2O:PbO:SiO_2$, the potash levels are substantially greater than would be used in modern manufacture.

The explanation of the compositional imbalance of these glasses is of some interest to the historian of chemical technology. Whenever glassmaking is in an ascendency, the glassmaker seeks technological means for improving the quality of his wares. In attempting to make more nearly colourless glass, 'cristallo' in the case of Venice, it was recognized that the purification of raw materials would have a beneficial effect. When leaching and recrystallization processes were introduced for the purification of plant-ash alkalis, this would have had the effect of lowering the concentrations of calcium, magnesium, and aluminum in the resulting alkali, because these elements have a tendency to be present in less soluble chemical forms than the soda and/or potash. Consequently, when purified alkali was used for making glass, the resulting product would have been deficient in lime, magnesia, and alumina. Such glasses then would have unstable compositions until the glass technologists of the day became aware of this effect and compensated for it by adding additional lime in the form of some other ingredient. The net result in the interim would have been the production of purer and possibly more nearly colourless glass, which would have been susceptible to crizzling in the years to follow. There is ample evidence, in fact, that this is just what did happen in the descriptions of Neri regarding the purification of alkali as well as in the story of Ravenscroft's perfection of his lead-glass compositions [4]. We have under way some experiments with barilla plant ashes to verify this.

This effect would have been magnified if a greater percentage of alkali were used in the basic formulation, as might have been done in Venice in an effort to produce a glass with a longer working range, that is, a glass which would remain softened for a longer time and allow the glassmaker to perform the more elaborate manipulations required to make complicated decorative forms.

In connection with the chemical compositions, it is worth commenting upon a common misunderstanding. One often hears the remark that it is the pink glasses which tend to crizzle, and there are, indeed, a great many crizzled glasses which have a pronounced pinkish colour. However, this pink colour is confined to the crizzled surface of the glass and the objects were initially colourless. Since manganese was often used as a decolorant, or might even have been present in some of the plant ashes, many early glasses contained manganese. When these glasses are attacked by water and alkali is leached out, the structures are opened up and the manganese becomes oxidized, yielding a pink colour in the crizzled layer. That this is true has been verified by the fact that when a crizzled layer is removed from one of these pink objects, the remaining glass is perfectly colourless.

3. ELECTRON MICROPROBE ANALYSES

Electron microprobe analyses of five of the glasses appearing in Table 1 were carried out by W. T. Kane and T. W. Bierweiler of Corning Glass Works. The analyses were made on small samples of glass removed from each of the objects. The samples were mounted in cross-section so that both the crizzled layer and the unaffected glass were exposed for analysis. Individual analyses of both regions on all samples were made for silicon, sodium,

	Glasses susceptible to crizzling				
	XS	XT	XU	XV	PP
SiO_2	73.5	75.5	75.0	65.0	75.8
Na_2O	22.0	—	—	—	0.1
K_2O	—	20.0	20.0	20.0	18.7
CaO	2.0	2.0	1.0	1.0	1.30
MgO	1.0	1.0	—	—	—
Al_2O_3	1.0	1.0	1.0	1.0	0.2
PbO	—	—	3.0	13.0	2.25
MnO	0.5	0.5	—	—	—
As_2O_3	—	—	—	—	1.65
Prototype	1050 (French)	449 (French)	457 (Venetian)	461 (Venetian)	457 (Venetian)

Table 3 contains compositions of synthetic mediaeval stained glasses also prepared by Dr Erickson. There are seventeen such glasses in the table. Their prototypes were groups of glasses, analysed by the author, from York, Nürnberg, and the Zerek Camii [5]. Series were also prepared to test various compositional effects on properties related to durability and weathering characteristics. The glasses represent variations in concentrations of Na_2O/K_2O, P_2O_5, MgO, and CuO; the effects of colour on both stable and durable glasses; and the duplication of an extremely interesting group of lead-containing mediaeval glasses. Some of these glasses have been used by Mr Bettembourg* in his research. We have carried out weathering and durability tests on several of these synthetic stained glasses, but they will not be discussed here, since they are beyond the scope of this paper.

5. WEATHERING AND DURABILITY TESTS

Samples of the synthetic corrosible glasses (XS, XT, XU, and XV) were subjected to three types of testing. These were a miniature powder test, weathering cabinet exposure and autoclaving. All the testing was carried out by P. B. Adams, H. V. Walters, and M. L. Nelson of Corning Glass Works using their routine testing procedures.

Since the details of the individual tests are rather complicated, we shall only outline the procedures here, but further information can be obtained by writing to Mr Adams.** The powder test consists of a water treatment of powdered glass at 90°C for four hours. The weight of alkali extracted is then determined by chemical analysis. The weathering cabinet test consists of exposing small pieces of the glass to an environment of 98% relative humidity at 50°C, and making periodic inspections for surface damage, which is then expressed in a standard terminology. The autoclaving was carried out at 121°C, at 15 psi, for various lengths of time, with the glasses immersed in the liquid phase. Small polished plates of the glass were used for autoclaving. (Other variations of the conditions for the tests were also used for exploratory purposes.)

The first two tests were used for evaluation of the durabilities of the glasses. The conditions parallel standard glass-testing procedures, so the results can be used for comparison with more familiar types of glasses.

The autoclaving was undertaken to look for chemical cracking and for the investigation of hydration—dehydration effects. For the latter purpose, autoclaving served to introduce water into the glasses. Different samples of the glasses were then stored under different relative humidity conditions (at room temperature), to see what levels of relative humidity might successfully inhibit the dehydration which produces crizzling. (As will be shown below, this hydration—dehydration treatment produces a kind of deterioration which is indistinguishable from the crizzling seen on actual early glasses.) The results of the tests are summarized in Table 4.

Some of the findings of the tests are listed below, accompanied by our interpretations.

1. In the powder test, glasses XS and XU, the soda glass and the potash glass with the light lead concentration, showed very poor resistance to hydrolysis. Glass XV, the more heavily-leaded glass, shows a considerably better resistance; and XT, the potash-lime glass, is still better. In fact, the durability of XT approaches that of some of the poorer present-day commercial glasses. It is somewhat surprising that XT holds up as well as it does, but it indicates that the addition of even the small increment of CaO (from 1.0 to 2.0%) over XV brings about a marked increase in stability. In comparing the durabilities of XS and XT, it should be noted that although the concentrations of soda and potash are not very different on a weight-percentage basis, in terms of mole percent the alkali content of the potash glass is markedly less (13.7% vs. 21.5%). This undoubtedly accounts for much of its increased durability. The glasses appear to rank as follows, in order of increasing durability: (very poor) XS ≈ XU ≪ XV < XT (fairly stable).
2. In the weathering cabinet exposures, XS was by far the poorest, and XT again the best. While some commercial bulb glasses do not fare much better than XS in this test, container glasses are much more durable. The glasses appear to rank as follows in order of increasing durability: (very poor) XS < XU < XV < XT (fairly stable).

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potassium, calcium, and lead (where present). Concentration maps for each element on each glass were obtained so that it is possible to see how the concentration of each element varies over an area including the glass, the crizzled layer, and their interface. The maps covered areas of about 100 x 25 μm. Profiles for each element were also constructed to see how their concentrations varied along a continuous path from the unaffected glass out through the crizzled layers. The concentration maps and profiles established the following points, to which are added our interpretations.

1. In the four glasses which were heavily crizzled (nos. 449, 461, 1050, and 1498) the sodium and potassium were very greatly depleted in the crizzled layer, indicating that these two elements had been thoroughly leached out of the glasses and probably removed to a large extent from the surface by washing in the past.
2. The silicon appears somewhat richer on a percentage basis in the crizzled layer than in the unaffected glass. The enrichment is the result of the depletion of the alkali, and it is likely that the total quantity of silica present was about the same before and after the crizzling attack took place.
3. The calcium and lead contents appear to have been unaffected by the leaching process because they, as within the silica, are less soluble than the alkalis. (It would have been difficult, however, to detect changes in the calcium level because the concentration was low to begin with.)
4. A void space could be detected in the four crizzled specimens which clearly marked the separation of the crizzled layer from the glass beneath. The analysts likened the appearance of the profiles to a 'step function', showing extensive depletion of the alkali outside the fissure in the crizzled layer. In two instances a second fissure was revealed beneath the crizzled layer, but this underlayer does not show complete depletion of alkali, only a tendency towards lower concentration. This indicates that the hydration and leaching reactions have proceeded onward into the glass beyond the first fissure separating the depleted layer from the glass. This serves as a reminder that we are dealing with a dynamic system, and that the process does not stop when a flake of crizzling products appears.
5. In a few places, highly localized concentrations of alkali showed up indicating that alkali had redeposited within the fissures. We believe we have also seen such deposits during microscopic examinations of various crizzled glasses. This would be the fate of alkali which had been exchanged by water but had never been washed off the glass during its history of human handling.
6. In sample no. 4011, a glass which showed only incipient crizzling, the alkalis have not been entirely removed from the glass, and the profile does not show the step-like appearance of the crizzled glasses. The alkali concentration shows a gradual depletion gradient sloping down from the unaffected glass to the surface. The profile has the character of a diffusion front. There is some evidence of the beginning of a fissure within the hydrolysing layer. (In anticipation of suggestions which might be prompted by the demonstrated presence of some alkali within this layer, we regard it as doubtful that the process could be reversed successfully and the glassy structure of the layer reconstituted by reintroducing alkali.)
7. The overall thicknesses of the reaction zones as seen through a light microscope measure between 45 and 100 μm, but the microprobe profiles yield additional information. From the spacing of the fissures in the profiles, the thicknesses of the separated layers (the crizzled layers) can be estimated. They range from 25 to 55 μm. In three of the four 'already crizzled' glasses, the layer which had separated is totally depleted in alkali. In the fourth glass, the front of the reaction zone is still within the crizzled layer, and the undersurface of the crizzled layer is quite rich in alkali. In the three instances where the reaction zone had advanced beyond the fissure separating the crizzled layer, the depletion/hydration fronts had penetrated between 40 and 80 μm from the 'original' surface. On the piece showing only incipient crizzling, the depletion/hydration front had penetrated 23 μm into the glass.

If one takes the thicknesses of the crizzled layers and ages of the glasses at face value, the hydration/alkali depletion rate of these five glasses averages out to about 0.3 μm per year. Compared to ancient glasses which are heavily weathered (those suitable for layer-counting), this is not as rapid a rate of hydration. The latter glasses hydrate at a rate of about 0.5–3.0 μm per year. However, lightly weathered ancient glasses, such as those showing iridescence, hydrate more slowly than the crizzled glasses. Iridescent Roman and Islamic glasses hydrate at a rate of only about 0.1 μm per year or less.

4. SYNTHETIC CORROSIBLE GLASSES

In order to learn more about the crizzling process a series of synthetic glasses was prepared. The compositions of the glasses, which are given in Table 2, were patterned like those obtained from the chemical analyses of four of the early glasses reported in Table 1. The glasses were prepared by A. A. Erickson of Corning Glass Works and his co-workers. The compositions given in Table 2 are theoretical values calculated from batch compositions, but chemical analyses of the glasses match them closely. These glasses were used for several types of experiments.

Table 3. Compositions of synthetic stained glasses

	QQ	QR	QS	RC	RD	RE	RF	VS	VW	VX	VY	VZ	FE	FF	FG	FH	FI
SiO_2	58.5	55.5	66.0	60.0	54.0	48.0	48.0	63.0	63.0	56.7	56.7	56.7	50.0	48.4	63.0	61.0	69.5
K_2O	8.5	18.5	1.5	20.0	18.0	16.0	16.0	18.0	—	16.2	16.2	16.2	17.0	16.4	12.5	12.0	1.5
Na_2O	3.0	0.5	14.0	—	—	—	—	—	18.0	—	—	—	3.0	2.9	1.5	1.5	14.0
CaO	16.0	19.0	10.0	20.0	18.0	16.0	16.0	18.0	18.0	16.2	16.2	16.2	16.0	15.4	12.0	11.6	12.0
MgO	7.0	2.5	1.4	—	—	—	—	—	—	—	10.0	—	7.0	6.9	4.0	3.9	—
Al_2O_3	1.0	1.0	2.0	—	—	—	—	—	—	—	—	—	1.5	1.5	1.5	1.5	1.5
P_2O_5	4.0	1.0	—	—	—	—	—	—	—	10.0	—	—	4.0	3.9	4.0	3.9	—
Fe_2O_3	1.0	1.0	1.0	—	—	—	—	1.0	1.0	0.9	0.9	0.9	0.5	0.5	0.5	0.5	0.5
MnO	1.0	1.0	1.0	—	—	—	—	—	—	—	—	—	1.0	1.0	1.0	1.0	1.0
CuO	—	—	3.0	—	—	—	3.0	—	—	—	—	10.0	—	3.0	—	3.0	—
CoO	—	—	0.1	—	—	—	—	—	—	—	—	—	—	0.1	—	0.1	—
PbO	—	—	—	—	10.0	20.0	17.0	—	—	—	—	—	—	—	—	—	—
Prototype	York	Nürnberg	Zerek Camii	K_2O base glass	PbO effect	PbO effect	PbO effect	K_2O base glass	Na_2O-K_2O subst.	P_2O_5 effect	MgO effect	CuO effect	Unstable	Unstable, blue	Durable	Durable, blue	Na_2O-K_2O subst.

3. The autoclaving produced chemical cracking [6] in XS even after only short durations. XU and XV developed a surface haziness, while XT showed no apparent change. The glasses appear to rank as follows, in order of increasing durability: (very poor) XS < XU < XV ≪ XT (apparently stable).

Table 4. Results of durability tests

	XS	XT	XU	XV
Powder test*				
Alkali extracted (Wt —% of glass)				
Na_2O	0.48	—	—	—
K_2O	—	0.057	0.71	0.16
Alkali extracted (Mmole/100 g glass)				
Na_2O	7.7	—	—	—
K_2O	—	0.61	7.5	1.7
Weathering cabinet exposure**				
Time required to breakdown	2 wks	8 wks	4 wks	6 wks
Chemical cracking***				
Days required	1	none occurs	≈8	≈15

* Sample wt ≈1 gram, adjusted to constant surface area from density; —40 to +50 mesh; 5 ml H_2O. Run for 4 hours at 90°C.

** 98% RH, 50°C. Breakdown = Obvious damage under inspection without magnification.

*** 2.5 x 2.5 x 0.1 cm polished plates in 285 ml H_2O, 95°C, 15 psi, for varying times.

6. INFRARED ANALYSES

Infrared reflectance and transmission spectra were taken for several samples of autoclaved glasses and their untreated counterparts. The spectra were run by H. Hoover and B. Butler of Corning Glass Works.

Reflectance spectra in the 8-12 μm region established clearly that the autoclaved glasses had been depleted in alkali because they showed a sharper reflectance peak than the anhydrous glasses. The shift indicates less disturbance of the Si—O—Si bonds by alkali or other modifiers. It is noteworthy that this was true even of the glass XT, which showed no visible evidence of alteration after the autoclaving.

Infrared transmission spectra in the 2-5 μm region indicated the presence of large quantities of beta-hydroxyls, or loosely-bound water. A sample of glass XV which had been hydrated through autoclaving was crizzled by heating it to 135°C for 1½ hours. A spectrum of the crizzled glass fell in between the spectra for the hydrated glass and an anhydrous control, indicating that although a significant amount of the beta-hydroxyl was removed, a significant amount still remained after the crizzling was induced.

Infrared spectra of an autoclaved sample of XV (30 minutes at 121°C) were taken progressively as the hydrated surfaces were polished away. By this means it was possible to estimate that this particular hydration process had hydrated this glass to a depth of approximately 20 μm, somewhat less than the thicknesses of the crizzled layer on early glasses.

Further infrared work is being conducted in an attempt to identify the different states of binding of water within the hydrated glasses [7].

7. HYDRATION—DEHYDRATION EXPERIMENTS

Several experiments have been carried out with a view to duplicating crizzling in the laboratory. Among these were preliminary experiments which demonstrated that by heating certain types of actual historic glasses (but not all types) to temperatures between 100° and 150°C, severe surface crizzling can be produced. These glasses were of diverse origins, including Roman glass from Karanis, some specimens of mediaeval stained glasses and eighteenth century vessel fragments. Other investigators have had similar experiences [8]. With this in mind, several pieces of synthetic glasses having corrosible compositions were held over water or immersed in water at 85°C for varying times and then dehydrated. It was found that the dehydration could be accomplished either by warming the glass to 50-65°C or by placing it in a desiccator. By various combinations of experimental conditions, several such glasses developed surface crizzling identical to that observed on early objects of crizzled glass. It might be added that some of the synthetic mediaeval stained glasses behaved similarly under these treatments.

We next set out to determine what levels of relative humidity, at room temperature, would inhibit the dehydration of hydrated glasses so as to arrest the development of crizzling. Experiments were carried out with the four synthetic glasses XS, XT, XU, and XV. In addition, two actual early objects were sacrificed for this

experiment. These experiments were carried out by M. L. Nelson and H. V. Walters. A similar series of experiments was conducted by the author in the Museum.

Small polished plates of the four synthetic glasses were hydrated by autoclaving at 121°C and 15 psi with total immersion in water. Various autoclaving times were used. After drying in air, the hydrated glasses were placed in glass chambers (actually desiccator jars) which maintained constant internal relative humidities established by saturated salt solutions in the bottoms of the chambers. The relative humidities were monitored with an electric hygrometer. The humidities were: 1%, 25-30% (ambient laboratory conditions), 40%, 72%, and 100%. (The samples in the 100% chamber soon became covered with droplets of condensed water.) Although the samples selected for the experiment were autoclaved for different times, all were similar in that after the autoclaving they showed no surface damage detectable by the unaided eye. After varying intervals of time, extending from a few days up to several weeks, many of the glasses developed crizzling. At the time of writing (March 1975), some samples still have not crizzled. The results are summarized in Table 5.

Table 5. Effect of storage conditions on hydrated glasses

Glass	Percentage of glasses which ultimately crizzled*				
	1%RH	25-35%RH	40%RH	72%RH	100%RH
XS	100%	17%**	0	0	0
XT	100	40	40	0	0
XU	100	100	100***	50***	0
XV	100	100	12	0	0
% crizzled irrespective of composition	100%	65	38	12	0

Duration of experiment to date: 11 Sept. 1974 – 17 Jan. 1975
Total number of samples used: ≈110

* The times required to develop crizzling varied widely. Some samples crizzled within a few days, others required several weeks.
** Of the balance, they might not all have been hydrated.
*** Hydration might have been excessive.

Some other experiments

Glass	Treatments	Results
XS	1. Imm. water, 85°C, 78 hrs	Little surface change
	2. Storage at: 0%RH	Crizz. after few days
	31%	No change after 35 mos.
	75%	No change after 35 mos.
	100%	No change after 35 mos.
	3. Storage at: 0%	All show crizz. after 9 hrs
XS, XT, XU, XV	1. Imm. water, rm temp., 35 mos.	XS, XU – Incip. crizz. XT, XV – No change
	2. Storage at: 0%RH	XS, XU, XV – Crizz. after 9 hrs XT – Start crizz.(?) after 2 wks
1823	1. Imm. water, rm temp., 35 mos.	No change
	2. Storage at: 0%RH	Start crizz. after 90 min. Crizz. after 16 hrs
	12%RH	Start crizz.(?) after 2 wks
1823	1. Storage at: 100%RH Rm temp., 35 mos.	No change
	2. Second storage at: 0%	Crizz. after 16 hrs
4011	1. No laboratory hydration	
	2. Storage at: 0%RH	Crizz. within 24 hrs
	12%	Start crizz.(?) after about 4 wks
	21%, 34%, 52%, 70%, 100%	No change yet after 11 wks

A similar set of hydration – dehydration experiments was started in 1971, but most of the apparatus, glasses, and records were destroyed in the flood which struck the Museum in June 1972. Fortunately, there were some survivals which now show interesting results. Samples of glass XS were hydrated by immersion in water at 85°C

for 78 hours. The samples showed little change after the hydration step. They were then stored for eleven days at humidities of 0%, 31%, 75%, and 100%. The piece stored at near-zero percent crizzled severely; the others did not show much change. They were left in the same chambers for 35 months and little further damage occurred. They were then transferred to a near-zero humidity chamber and within nine hours all developed crizzling.

In another experiment, pieces of glasses XS, XT, XU, and XV were given no high temperature hydration, but just left to hydrate in distilled water at room temperature for 35 months. XS and XU developed some chemical cracking and incipient crizzling, respectively; but XT and XV showed no surface alteration at all. However, when placed in a near-zero humidity, all except XT developed severe crizzling within nine hours. (XT again proved to be surprisingly durable, as it did in certain other experiments.)

The experiments carried out on the two early glasses, nos. 1823 and 4011, offer a different approach to the problem and avoid the difficulties posed by the use of autoclaving to hydrate the glasses.

Glass no. 4011 is an engraved Silesian goblet made in about 1710-30. The piece shows typical incipient crizzling (Figure 3). The foot of the goblet had been broken in the distant past, and the piece was not considered to be of outstanding historical importance. Therefore, Mr Jerome Strauss, who owned the object for some years, donated it to the Museum for use in our experiments, feeling that the information to be gained from sacrificing parts of the glass would prove to be more valuable than the glass itself. Samples were sawed from the rim above the engraving. They were carefully photographed under reproducible lighting conditions, and photomicrographs were taken to record the original state of the incipient crizzling. One small piece was used for chemical analysis, and several of the others were placed in chambers for storage at known humidities.

Once again the humidities of the chambers were controlled by saturated salt solutions, except for a desiccating chamber employing silica gel for a near-zero humidity, and one containing distilled water for 100% humidity. No attempt was made to control the temperature. Instead, ambient room temperatures prevailed. The humidities, as measured with an electric hygrometer, are: ≈0%, 12%, 21%, 34%, 52%, 70%, and 100%.

It was found that the piece of object no. 4011 placed in the chamber at near-zero humidity became severely crizzled within 24 hours (Figures 4 and 5). The piece in the chamber at 12% seems to have begun to show signs of developing crizzling at the time of writing, which corresponds to an elapsed time of about four weeks at 12%. None of the samples at other humidities have changed.

Glass no. 1823 is a small green bottle made in 1971 at the Jamestown, Virginia, factory. It was sent to the author for examination because it developed a slippery surface feeling shortly after manufacture. After a chemical analysis showed an excessive alkali content to be the cause, parts of this bottle were also sacrificed for hydration--dehydration experimentation. Fragments were stored for four months at ambient conditions in Corning and then stored in a 100% humidity chamber for 35 months. Another fragment of the same glass was immersed in distilled water for 35 months. Neither glass showed any visible signs of surface deterioration at the end of these hydration steps. Samples of these same fragments were then placed in a near-zero humidity chamber, and others in a 12% chamber. Within 90 minutes of being placed in the near-zero chamber, the samples showed beginning stages of crizzling. They were left overnight in the chamber and had become severely crizzled by the next morning after a total of 16 hours at near-zero humidity. One of the samples in the 12% chamber appears to be developing slight crizzling after about two weeks, at the time of writing.

It is conceded that the logic which is about to be followed is weakened by a few significant defects, but even with these in mind it is worth pursuing. In some of the experiments outlined above, the hydration conditions were chosen arbitrarily and were not always the same for each glass, so care must be exercised in comparing the behaviour of one glass with another. Moreover, the autoclaving used to hydrate the glasses was a rather drastic treatment. It can be argued that the hydrated state induced by autoclaving might not be the same as that brought about by the slower 'natural' hydration produced by the action of atmospheric water vapour over centuries at room temperature. But nonetheless, these are the only data we have, and in effect this same defect marks the interpretation of any accelerated ageing test, so it is familiar to all conservators.

From the results in the first part of Table 5, it could be concluded that hydrated glasses of this type will crizzle rapidly if stored at near-zero humidity, but will not dehydrate (not rapidly) at humidities of about 70% or greater. In the range of 25-40%, many such glasses will crizzle; between about 40-70%, some glasses will crizzle.

The findings presented in the second part of Table 5 represent longer term experiments and different hydration processes, some of which eliminate the onus of accelerated ageing. From the results of these experiments, it can be inferred that glasses hydrated by exposure either to hot water for short times or to cool water for a matter of years will retain their moisture for long periods when stored at humidities between 30-100%, but that they rapidly give up that moisture and become severely crizzled if transferred to a near-zero humidity environment.

The experiment most closely simulating actual museum conditions, that involving the Silesian goblet, demonstrated unequivocally that storage of a glass showing incipient crizzling at a near-zero humidity will provoke severe crizzling within a matter of hours. The data on the Jamestown glass substantiate this finding. It remains to be seen whether relatively rapid crizzling can also develop on susceptible glasses in the range of about 25-40% relative humidity, and we have set up long-term experiments to answer this question.

8. STORAGE CONDITIONS AND CASE DESIGN

From all of the foregoing, it is apparent that dehydration is the cause of the advancement of incipient crizzling into full crizzling, and it is obvious that very low humidity conditions must be avoided if susceptible glasses are to be protected. The next point to be established is just what constitutes an optimum range for safe storage.

It is somewhat disquieting that dehydration occurs at relative humidities as high as 40-60% and that only levels

of 70% or greater appear to hold hydration water in the experimental glasses. It is likely, however, that this is because the water had been driven into the glasses under rather drastic conditions. It is doubtful that early glasses with incipient crizzling dehydrate significantly in the 40-60% range. After all, such glasses must already have spent much of their existence in humidities within that range and have not gone over to full crizzling. We are prepared to assume, then, that the 40-60% range is safe.

Storage at very high humidities with a view towards keeping water in might then accelerate the hydration of the glasses and contribute to their ultimate deterioration, to say nothing of the impracticalities posed by possible mould growth, condensation, etc. We conclude, therefore, that from the viewpoint of protection against dehydration:

1. The 70-100% range is unnecessarily high and undesirable.
2. The 40-60% range is safe.
3. The 25-40% range remains open to question and should be studied in terms of years-long storage experiments on actual early glasses.
4. The 0-25% range is dangerous, in fact very dangerous at the lower end.

The situation, then, can be reduced to questioning whether there is anything else that can go wrong in the 40-60% range.

In 1959 Organ and Bimson [9] dealt with a related – but not identical – problem to that being discussed here. They recommended that for safe storage unstable glasses should be kept dry, specifying that by dry they meant at a relative humidity below 42%. The reasoning was that at humidities below 42%, potassium carbonate (the ultimate form of alkali leached out of potassium glasses) is not hygroscopic. This reasoning is certainly sound for the types of glasses they were considering, that is, 'weeping' or 'sweating' glasses, and the validity of their recommendation seems to have been borne out by actual experience. In the intervening years, large numbers of 'weeping' glasses from the collections of the British Museum were stored in cases where the humidity was kept at or below 42%. In a recent visit to the British Museum, the author accompanied Ms Bimson and Mr Hugh Tait on an inspection of the glass involved. It was found that few of the glasses in the cases had the slipperiness to touch which characterizes 'weeping' glasses. (Those examples which were found to be somewhat slippery were Venetian glasses which might have been soda glasses instead of potash glasses.)

A troublesome question then arises as to whether the dehydration rate of glasses with incipient crizzling might become fast enough to provoke full crizzling if they are stored at humidities below 42%; or, indeed, could the same thing happen to 'weeping' glasses? It is probably artificial to treat these as two entirely different kinds of glasses. Mr Tait and Ms Bimson did not recognize among the glasses in the British Museum cases any which they could say had become more deteriorated during the years of storage in those cases. However, since so many glasses were involved, and since no photographic records of the original states of the objects were at hand, it could not be determined with certainty whether or not any of these glasses had become more crizzled.

With this in mind, we can turn to the practical problem faced by The Corning Museum of Glass, the protection of glasses which show incipient crizzling. There are perhaps 50 such objects in our collections. Our primary object is to arrest any further deterioration brought on by dehydration and, if possible, to minimize the continued uptake of moisture. (It is recognized that improving storage conditions will not correct the damage already inflicted upon the glass.) Ideally, one would assume the safest condition to be a humidity level where a steady state could be established under which neither the hydration nor dehydration reactions would progress. Since it is not likely that we could now arrive at a single level which would satisfy steady-state conditions for so many different glasses, we have elected to err on the side of hydration, feeling that this offers less hazard to the glasses than dehydration. It might further be guessed that, to ensure that dehydration will not occur, the humidity should be in approximately the range to which the glasses had become accustomed in their early histories.

For these reasons, we have decided to aim initially for case control at the 45-55% relative humidity range, with provisions for sufficient adaptability to allow the humidity level to be shifted somewhat in either direction. (For example, if persistent slipperiness developed upon the surfaces, we might want to drop slightly below the 42% level.)

A committee of conservators was convened to offer advice on our system design and case construction. The committee consists of Robert Feller, Lawrence Majewski, Susanne Sack, and Nathan Stolow. The designs have not yet been completed, but several pivotal decisions have been made. The resultant system contains three main components: the cases, controlling devices, and a regenerating unit.

The cases themselves will be sealed, with access through one door. One face, at least, will be glass or plexiglas for exhibition purposes. Proper gasketing will be very important. The case will contain some humidity-buffering material to offset variation caused by changes in temperature. Since the temperature of our galleries can be controlled, no special temperature control will be introduced in the cases.

Special care will be given to lighting the cases. The lighting will be external and properly situated so as not to cause a heat build-up, and infrared absorbing shields will be used. The deleterious effects of spotlighting objects for dramatic exhibition are appreciated by conservators but not by all curators or collectors. The effects of heat build-up can be very serious on certain types of glass, for example, glasses with incipient crizzling, painted surfaces, or weathering products. In an experiment conducted in our museum, flat plates of glass were placed on a wooden pedestal painted black and lit with two 12-volt automobile lamps at a distance of about one metre. The temperatures of the glasses were measured by thermistor probes placed in hollowed-out depressions in the glasses. At one point within a piece of glass, a temperature of 67°C was measured. Temperatures of this level could seriously endanger glasses of the sorts mentioned and should never be tolerated.

The cases will be connected to controlling units containing trays of silica gel which will have been equilibrated previously to the target relative humidity, perhaps 45% to start with. It was decided that silica gel would be used

as the controlling medium because of its inertness, low sensitivity to temperature change, regenerative qualities, and adaptability to different levels of humidity control. Circulating devices with proper safety controls will be used to assure adequate circulation between the control units and the cases. A remote recording thermohygrograph will monitor the relative humidity and temperature through sensing probes. A separate re-equilibrating unit in our workroom will be used to regenerate the silica gel as required.

It is expected that, if the sealants are good and the cases are not opened frequently, the system will remain stable for some months at a time. One of our major goals is to install a system which will operate with a minimum of maintenance and will be as free as possible of annoyances caused by failures of mechanical or electrical parts. For this reason, which may appear paradoxical to some readers, the Museum has elected not to install a fully-automated system. Our belief is that the more elaborate a system becomes mechanically, the more things there are to go wrong.

It is hoped that, through proper design and construction of these cases, our glass with incipient crizzling will be safely preserved throughout the coming years while we attempt to devise treatments which will restore chemical stability to these glasses, instead of just maintaining a delicately-balanced metastable state.

ACKNOWLEDGEMENTS

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THE YELLOWING OF EPOXY RESIN ADHESIVES: REPORT ON HIGH-INTENSITY LIGHT AGING

Jane L. Down

Abstract—Various room-temperature-cure epoxy resin adhesives suitable for use in glass conservation were tested for their tendency to yellow under high-intensity light. The results were extrapolated to representative museum conditions, taking into account both light- and thermally-induced contributions to yellowing. Life expectancy estimates, the length of time for a thin film of epoxy to yellow unacceptably, were obtained for each adhesive. Although the majority of products demonstrated an unacceptable level of stability, a few formulations were identified with less tendency to yellow than others. Recommendations for the use of specific epoxy resin adhesives are given.

1 Introduction

With the advent and use of room-temperature-cure epoxy resin adhesives for the repair of glass artifacts, many difficulties in bonding glass have been resolved [1]. The inherent tendency for epoxy resin adhesives to yellow with time has precluded their wider acceptance in conservation. Research is continuing and there have been many new developments. A recent study by the author succeeded in identifying some formulations that showed less tendency to yellow than others under natural dark aging [2]. This study discussed only the contribution to yellowing of ambient thermal reactions. A study on the light aging of seven epoxy resins for stained glass conservation, reported by Tennent [3], identified three resins that yellowed least on exposure to light. Evidence was presented that dibutyl phthalate (DBP) plasticizer and alkyl phenol accelerator additives tend to promote yellowing and that varying the component ratios alters yellowing rates. A more recent paper by the same author [4] identified two chromophores in epoxy resins that could be responsible for the observed light-induced yellowing.

Other research studies on the light aging of epoxy resins have followed carbonyl group formation using infrared analyses and have found that the nature of the resin and hardener and the light exposure conditions influence its development [5–7]. Mechanisms have been proposed to account for carbonyl group formation due to light aging [8]; however, Lee [9] noted that carbonyl group formation did not relate to yellowing. In the same paper, Lee indicated that light-induced yellowing of epoxy resins was influenced by the following hardener characteristics: nitrogen groups adjacent to aromatic rings, ethylene groups rather than methylene or propylene groups separating nitrogen groups, the number of amine functional groups and trace impurities. Kelleher [10] suggested that light-induced yellowing was caused by the formation of a conjugated structure in the bisphenol-A portion of the resin. Noskov [8] proposed that pigmentation was due to transformations in the fragments of chains containing aromatic rings.

The identification of the mechanism and chromophores of light-induced yellowing of epoxy resin adhesives would be invaluable in choosing a suitable compound for use in conservation. Synthesis of a superior epoxy resin that could be made readily available would be ideal. Although the ideal solution does not yet exist, work in this area is progressing. A more practical alternative, at present, is to identify commercially-available epoxy products that yellow slowly. This paper deals with this practical alternative. Although previous studies have compared the aging of some epoxy resins, the product selection was limited. This paper reports data on a total of 47 products with varying chemical compositions.

2 Experimental methods and results

2.1 *Experimental procedure*

Seventy manufacturers were asked for samples of epoxy resin adhesives suitable for the repair of glass artifacts. The criteria specified were that the epoxy should remain clear and colourless and that the mechanical strength of the bond should remain relatively high even after 50–100 years of natural aging. Although many were dubious that any epoxy would remain colourless after this length of time, 24 companies participated and a total of 47 products was tested.

Sample preparation and absorbance measurement have been described previously [2]. Samples were first measured for absorbance at 380 and 600nm prior to aging in an Atlas Weather-Ometer equipped with a 6500-watt xenon arc lamp and infrared absorbing filters. Constant irradiation was ensured by following the manufacturer's recommendation to increase lamp wattage at predetermined intervals. These exposure conditions simulated noon summer sunlight filtered through normal window-glass (i.e., cut-off at 300nm). The temperature and relative humidity inside the chamber were maintained at ideal museum conditions, 22°C ± 1°C and 50% ± 5% respectively. The black panel temperature was approximately 35°C.

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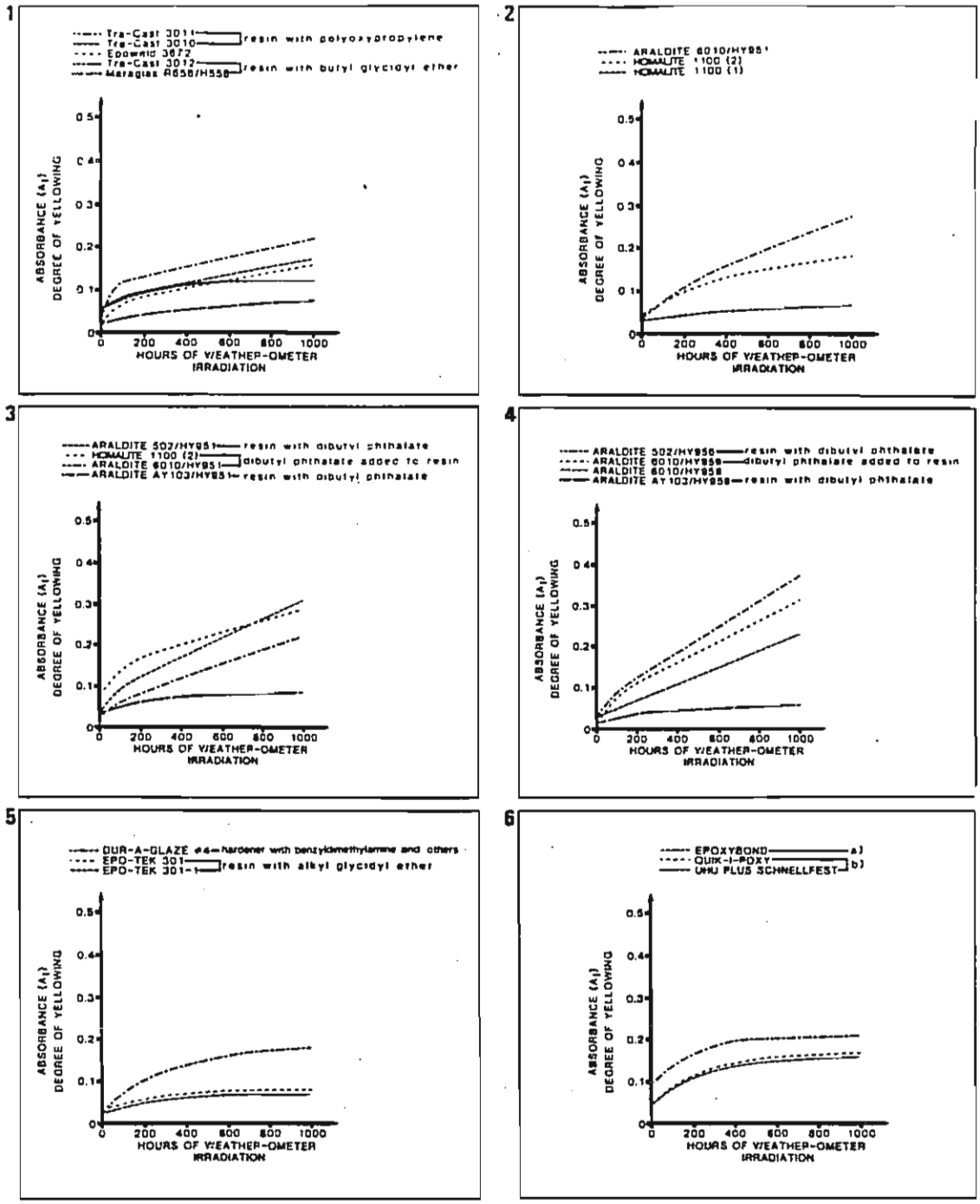
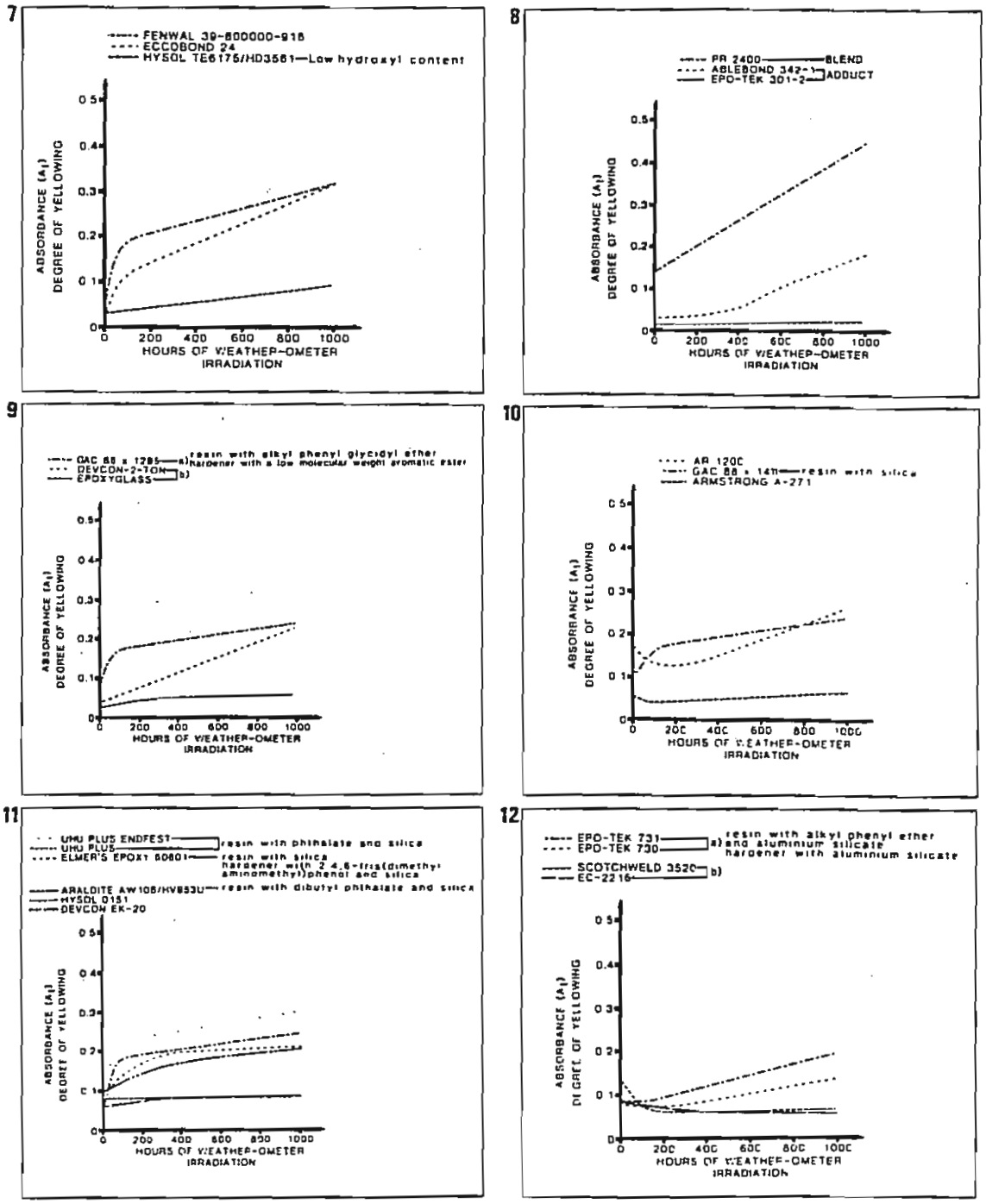
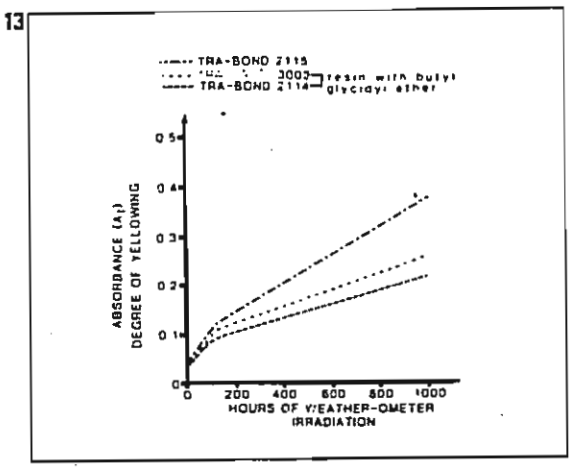
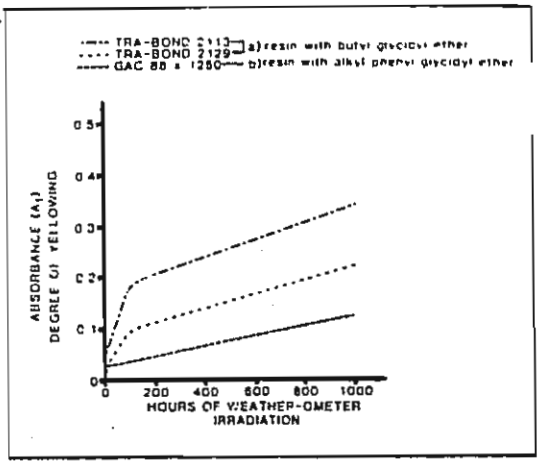


Figures 1–6 The effect of high-intensity light aging on the yellowing of epoxy resin adhesives with (1) diglycidyl ether of bisphenol A (DGEBA) resins and modified amine hardeners; (2) DGEBA resins and triethylenetetramine hardeners; (3) DGEBA resins containing dibutyl phthalate plasticizer and triethylenetetramine hardeners; (4) DGEBA resins and hardeners composed of a mixture of triethylenetetramine, tetraethylenepentamine and higher polymeric ethylene amines; (5) DGEBA resins and trimethylhexamethylene diamine hardeners; (6) DGEBA resins and (a) an unidentified hardener, (b) polyoxypropylene diamine hardeners.

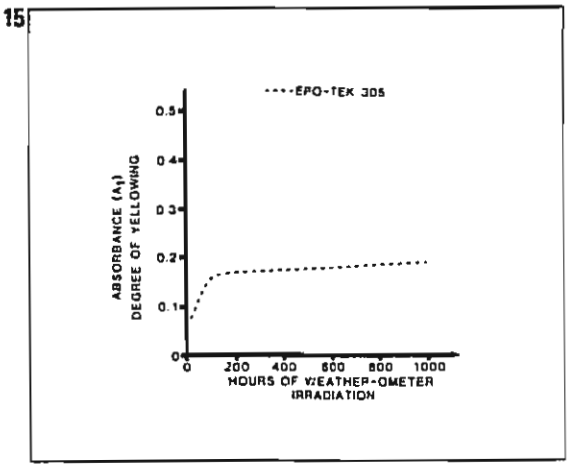


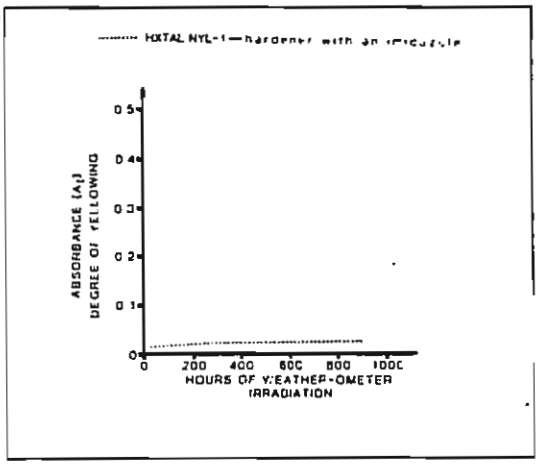
Figures 7–12 The effect of high-intensity light aging on the yellowing of epoxy resin adhesives with DGEBA resins and (7) hardeners composed of a blend or adduct of polyoxyethylene and a primary aliphatic polyamine; (8) hardeners composed of a blend or adduct of polyoxypropylene and an aliphatic polyamine. (9) (a) a hardener composed of a mixture of an aliphatic polyamine, (b) polyamine epoxy resin adduct hardeners. (10) fatty polyamide (very high amine value) hardeners; (11) fatty polyamide (high amine value) hardeners; (12) (a) hardeners composed of a mixture of an aliphatic polyamine and a fatty polyamide, (b) fatty polyamide hardeners adducted or blended with polyoxyethylene.





Figures 13, 14 The effect of high-intensity light aging on the yellowing of epoxy resin adhesives with DGEBA resins and (13) hardeners composed of polyoxyethylene blended or adducted with a polyamide epoxy adduct; (14) (a) amino-amide-phenyl glycidyl ether adduct hardeners, (b) polyoxypropylene-dicyandiamide blended or adducted hardener.





Figures 15, 16 The effect of high-intensity light aging on the yellowing of an epoxy resin adhesive with (15) a 1,2,3-tris(2,3-epoxypropoxy)propane resin and a trimethylhexamethylene diamine hardener; (16) an hydrogenated DGEBA resin and a hardener composed of a blend or adduct of polyoxypropylene and an aliphatic polyamine.

Samples were removed from the Weather-Ometer at specific time intervals and absorbance at 380 and 600nm was measured. Exposure was terminated after 1000 hours giving a total ultraviolet irradiation in the 300–400nm range of 35kWhr/m^2.

Since cross-sections of cured aged epoxies showed that yellowing was not a surface phenomenon but constant throughout the thickness of the film, absorbance data ($A_{(380nm)} - A_{(600nm)}$) were adjusted for each individual film thickness by standardization to a common thickness of 0·1mm, the approximate thickness of a glass glue joint, to obtain A_t [2]. A_t for each set of replicate samples was averaged. A_t is the measure of the degree of yellowing of an epoxy film at a specific time. Yellowing curves, plots of A_t versus time, were made for each epoxy product tested. These curves are shown in Figures 1 to 16 and are grouped in the figures according to the chemical composition of their resin and hardener, previously determined [2].

The use of the data obtained with intense irradiation to predict yellowing rates under typical museum lighting conditions is complex. This is because:

1 The contribution to yellowing from thermal

reactions which have been shown to be of equal or greater importance to light-induced yellowing cannot be ignored;

2 a linear relationship between yellowing and light intensity cannot be assumed.

2.2 *Thermal contributions to yellowing*

In comparison with typical environmental conditions that might be found in a museum, the exposure conditions used in our experiments would accelerate light-induced yellowing, not thermally-induced yellowing. Samples subjected to less severe museum lighting conditions would require a much longer time to absorb the same total radiation as Weather-Ometer treated samples. After such long periods of natural aging, the thermal contribution to yellowing could be significant. The interrelationship between light- and thermally-induced yellowing is complex. In the practical situation, it is impossible to make a meaningful prediction of the combined effect based on the results of the two effects taken separately because both bleaching by light and light-induced acceleration of thermally-produced yellowing were observed. The usual approach is to consider either light-induced or thermally-induced effects independently. This is valid only when thermally-induced effects are negligible in comparison to light-induced effects and vice versa. Since the contribution to yellowing of epoxy resins due to long-term thermal effects has been shown to be substantial [2], it was felt that they could not be ignored in the consideration of long-term effects of light.

In the absence of any known theoretical or experimental approach, the light-induced and thermally-induced values of yellowing were simply added together. In the final analysis, it did not make any difference in the selection of an epoxy since there were a few products that performed reasonably well under each set of circumstances and there was no reason to believe that they would behave any differently when exposed to the combined effects. The life expectancy of an epoxy given in this way may be some indication of how long it will take an epoxy to yellow unacceptably but there is no guarantee of the validity or accuracy of this prediction.

2.3 *Light intensity versus yellowing*

In order to add the light-induced yellowing values to the thermally-induced yellowing values, it was first necessary to convert the yellowing curves obtained from high-intensity light aging to represent yellowing under less intense museum lighting. This conversion is possible only if yellowing under less intense museum lighting can be shown to be directly related to yellowing under the xenon arc source and to the irradiation intensities of the light sources. This was shown to be true by investigating the relationship between yellowing, irradiation intensity and absorbed intensity.

The relationship between yellowing of epoxy resins and irradiation intensity of the xenon arc source was investigated in a separate experiment. Samples of the same cured epoxy were placed at two distinct distances from the xenon arc source giving two different irradiation intensities. The samples were exposed to the xenon arc source for several hundred hours and yellowing of the samples was monitored at regular intervals, as in the original experiment. Initial rates of yellowing of the samples were calculated and plotted against irradiation intensity. Examples of these plots can be seen in Figure 17. The resulting curves fell

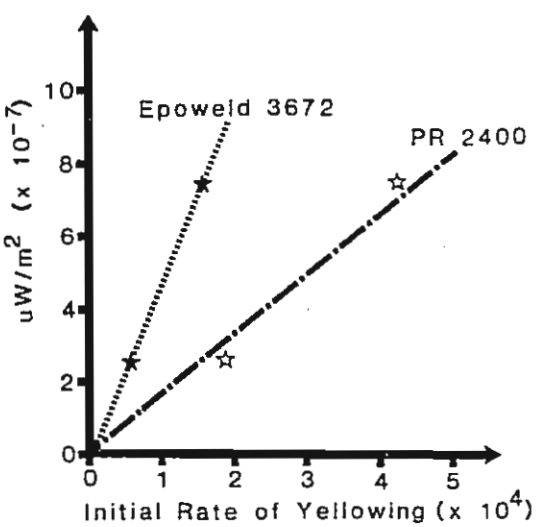


Figure 17 Irradiation intensity ($\mu W \cdot m^{-2}$) versus initial rate of yellowing of Epoweld 3672 and PR 2400.

through the origin and tended to be linear, indicating that yellowing is directly proportional to the irradiation intensity of the xenon arc source as represented by equation 1:

$$Y_x \propto I_x \qquad (1)$$

where Y_x = yellowing of epoxy resin under xenon arc source and I_x = irradiation intensity of xenon arc source.

Now, according to Beer's Law, the absorbed intensity (the actual quantity of light absorbed by an epoxy from any light source) is proportional to the irradiation intensity of the light source as represented by equation 2:

$$IA_x \propto I_x \qquad (2)$$

where IA_x = absorbed intensity by an epoxy resin from the xenon arc source.

By substitution (equation 2 into equation 1), it can therefore be shown that for the xenon arc source,

yellowing is directly proportional to absorbed intensity as represented by equation 3:

$$Y_x = c_x . IA_x \quad (3)$$

where c_x = a constant for the xenon arc source.

At this point, an implicit assumption is made that equation 3 holds true for any other light source as represented by equation 4:

$$Y_z = c_z . IA_z \quad (4)$$

where Y_z = yellowing of epoxy resin under light source z, IA_z = absorbed intensity by an epoxy resin from light source z, and c_z = a constant for light source z.

Now, in a separate experiment, the relationship represented by equation 5 was shown to hold true when illumination intensity (II) was held constant (i.e. $II_x = II_z$):

$$\frac{I_x}{I_z} = \frac{I_{uvx} . II_x}{I_{uvz} . II_z} = \frac{IA_x}{IA_z} \quad (5)$$

where I_{uvx} = proportion of ultraviolet in visible light—xenon arc source, I_{uvz} = proportion of ultraviolet in visible light—light source z, II_x = illumination intensity—xenon arc source, and II_z = illumination intensity—light source z.

The experiment involved obtaining spectral power distributions of three representative museum light sources and the xenon arc source and normalizing them to the same illumination intensity. The absorbed intensity of a few epoxy resins was calculated for each of the four light sources. The actual calculation of the absorbed intensity involved determining the area under the curve resulting from the multiplication of the absorbance spectrum of an epoxy by the normalized spectral power distribution. This was done in the region from 300 to 400nm, the region of greatest absorption of epoxy resins. Next the ratio A was determined, as defined by equation 6:

$$A = \frac{IA_x}{IA_z} \quad (6)$$

Finally, the proportion of ultraviolet radiatio (300–400nm)in visible light for each light source was determined and the ratio L was calculated, as defined by equation 7:

$$L = \frac{I_{uvx}}{I_{uvz}} \quad (7)$$

Table 1 lists the ratios L for various light sources and the respective A ratios for sample epoxies. It can easily be seen from this table that the absorbed intensity ratios are nearly identical to the proportion of ultraviolet radiation ratios. Thus, equation 5 is shown to be valid. By substituting equations 3 and 4 into equation 5, it can be demonstrated that yellowing under any other light source is related to yellowing under the xenon arc source and the irradiation intensities as represented by equation 8:

$$Y_x = \frac{c_x}{c_z} . \frac{I_z}{I_x} . Y_z \quad (8)$$

Thus, yellowing under the xenon arc source and irradiation intensities of the xenon arc source and other less intense museum light sources may be used to determine yellowing under these less intense light sources.

2.4 Determining life expectancies

Since most of the curves for high-intensity light-induced and thermally-induced yellowing were non-linear, their addition would be different depending on the lower light intensity situation chosen (e.g., filterr or unfiltered fluorescent lamps, filtered daylight, etc. For each situation chosen, it was first necessary to modify the high-intensity light-induced yellowing

Table 1 Comparison of the proportion of ultraviolet radiation ratios to the absorbed intensity ratios for two epoxy resin adhesives

Light source	*Proportion of UV radiation in visible light (300–400nm) μW/lm*	*Ratio L*	*Ratio A*			
			Epoweld 3672		*PR 2400*	
			Before aging	*After aging (413·8h Weather-Ometer)*	*Before aging*	*After aging (413·8h Weather-Ometer)*
Xenon arc lamp[a]	350	1	1	1	1	1
Daylight through window-glass[b]	variable ~350	1	1·3	1·5	1·3	1·3
Unfiltered fluorescent lamp (F40 CW)[c]	107	3·3	3·1	3·6	3·2	3
Tungsten lamp[b]	~75 or less	4·7	4·4	4·3	4·5	4·4

Spectral power distribution supplied by:
a J. B. Atlas Weather-Ometer Manual.
b THOMSON, G., *The Museum Environment*, Butterworth & Co. Ltd. London (1978), p. 160.
c GTE Sylvania Engineering Bulletin 0-341.

Table 2 Representative exposure conditions

Illumination level (lux)	*Proportion of UV radiation (300–400nm) μW/lm*	*Example in museum*
300	75	Safe illumination from incandescent or filtered fluorescent sources (e.g. 'ideal' museum environment)
1000	150	High illumination from average unfiltered fluorescent source (e.g. in a display case)
5000	350	High illumination from unfiltered daylight (e.g. near a north window)
23000	350	Direct sunlight (e.g. near a south window)

curve to represent the chosen situation using equation 8 (hereafter called a 'modified light-induced yellowing curve') and then add it to the natural dark aging curve previously determined [2]. Life expectancies were calculated from this derived yellowing curve (hereafter called a 'derived yellowing curve'). Since this was a somewhat lengthy procedure, the number of different lower light intensity situations was limited to four representative ones that might be found in a museum. These are described in Table 2. An example of the addition of a 'modified light-induced yellowing curve' to its natural dark aging curve is illustrated in Figure 18. Figure 19 shows all four of the 'derived yellowing curves' plus the natural dark aging curve for Tra-Cast 3011. Service life expectancy for a thin film (0·1mm) was estimated for every epoxy formulation using the 'derived yellowing curves' and is given in Table 3. Estimates will, of course, be shortened for thicker films and lengthened for thinner films. Standard 0·1mm films were used to allow comparison of one product with another. If thicker or thinner films are considered then estimates will change accordingly but the relative order will remain the same. The choice of absorbance values for slightly yellow and strongly yellow (0·1 and 0·25 respectively) was based on a yellowing acceptability evaluation test previously described [2]. Also given in Table 3 is the initial colour (A_0) of the epoxy formulation prior to any exposure. The lower the value of A_0 the less yellow the formulation.

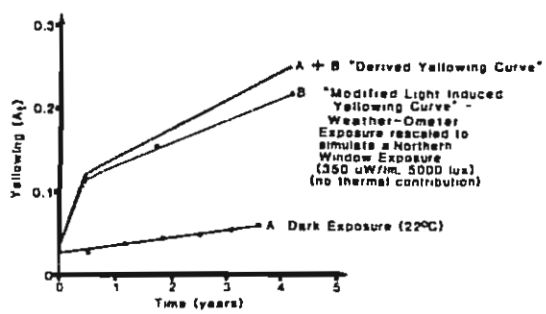


Figure 18 An example of a 'derived yellowing curve' produced from a 'modified light-induced yellowing curve' and a natural dark aging curve for epoxy Tra-Cast 3011.

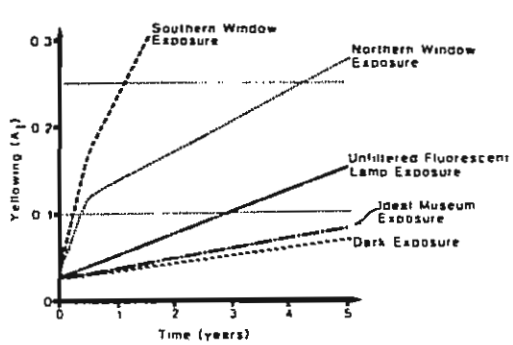


Figure 19 An example of the four 'derived yellowing curves' and the natural dark aging curve for epoxy Tra-Cast 3011

3 Discussion

The results presented in Figures 1 to 16 demonstrate that light-induced yellowing is not necessarily a linear function of time. In fact, there are four distinct types of yellowing curve:

1 linear (e.g., Hysol TE6175/HD3561);
2 autocatalytic [11], where the amount and rate of yellowing increase with time (e.g., Ablebond 342–1);
3 auto-retardant [11], where yellowing proceeds at a decreasing rate (e.g., Homalite 1100 (2));
4 initial bleaching, followed by a linear increase in yellowing (e.g., Scotchweld 3520).

The majority of epoxy products tested showed good, clear, initial colour (A_0) before aging, except the formulations containing a fatty polyamide type hardener, which were more yellow.

When both light- and thermally-induced yellowing were considered together, the results (Table 3) demonstrate that the intensity of light exposure dictates the service life expectancy of any epoxy resin. Under low intensity irradiation, such as would be found in an ideal museum environment, service life expectancy did

Table 3. Yellowing life expectancy estimates of epoxy resin adhesives (0·1mm-thick films) for various representative lighting exposure conditions found in museums

Epoxy	Initial colour (A_0)	Life expectancy (years)			
		Dark exposure [2] (22 °C)		'Ideal' museum exposure (75μW/lm; 300 lux; 22 °C)	
		Slightly yellow ($A_t = 0·1$)	Strongly yellow ($A_t = 0·25$)	Slightly yellow ($A_t = 0·1$)	Strongly yellow ($A_t = 0·25$)
Ablebond 342-1	0·064	35 ± 19	> 100 ± 54	27	78
AR 1200	0·188	0	2 ± 1	0	2
Araldite 502 HY951	0·018	< 1	3 ± 1	< 1	3
Araldite 502 HY956	0·016	3 ± 1	9 ± 1	3	9
Araldite 6010 HY951	0·024	< 0·5	3 ± 1	< 0·5	3
Araldite 6010/HY956	0·019	< 0·5	3 ± 1	< 0·5	3
Araldite 6010/HY951 + DBP*	0·017	< 1	2 ± 1	< 1	3
Araldite 6010/HY956 + DBP*	0·020	< 1	3 ± 1	< 1	3
Araldite AW106/HV953U	0·068	< 0·5	20 ± 7	< 0·5	16
Araldite AY103/HY951	0·031	1 ± 1	36 ± 11	1	31
Araldite AY103/HY956	0·016	40 ± 7	> 100 ± 21	33	100
Armstrong A-271	0·056	2 ± 1	19 ± 9	1	17
Devcon EK-20	0·049	< 0·5	13 ± 5	< 0·5	11
Devcon-2-ton	0·029	4 ± 1	26 ± 5	4	28
Dur-a-glaze #4	0·021	14 ± 2	41 ± 7	12	34
EC-2216	0·081	< 1	20 ± 3	< 1	20
Eccobond 24	0·023	5 ± 1	14 ± 1	4	12
Elmer's Epoxy	0·094	< 0·5	7 ± 1	< 0·5	7
Epo-Tek 301	0·025	8 ± 3	27 ± 13	5	17
Epo-Tek 301-1	0·018	10 ± 4	38 ± 15	8	30
Epo-Tek 301-2	0·017	18 ± 5	51 ± 13	17	49
Epo-Tek 305	0·031	2 ± 1	9 ± 1	2	8
Epo-Tek 730	0·075	< 1	11 ± 2	< 1	11
Epo-Tek 731	0·083	< 0·5	8 ± 1	< 0·5	8
Epoweld 3672	0·018	45 ± 11	> 100 ± 34	26	92
Epoxybond	0·077	< 1	12 ± 5	< 1	[illegible]
Epoxyglass	0·012	15 ± 2	42 ± 7	14	4
Fenwal 39-800000-918	0·028	9 ± 2	38 ± 10	5	19
GAC 88 × 1250	0·022	19 ± 3	57 ± 8	16	51
GAC 88 × 1295	0·068	1 ± 1	13 ± 1	1	10
GAC 88 × 1411	0·106	0	7 ± 1	0	7
Homalite 1100 (1)	0·030	2 ± 1	> 100	1	> 100
Homalite 1100 (2)	0·021	5 ± 1	17 ± 2	4	16
Homalite 1100 + DBP*	0·022	< 1	8 ± 3	< 1	7
Hxtal NYL-1	0·005	> 100 ± 17	> 100 ± 43	> 100	> 100
Hysol 0151	0·080	< 0·5	19 ± 3	< 0·5	19
Hysol TE6175/HD3561	0·037	6 ± 1	17 ± 2	6	17
Muraglas R658/H558	0·016	6 ± 1	18 ± 3	6	18
PR 2400	0·140	0	8 ± 2	0	6
Quik-i-poxy	0·041	3 ± 1	12 ± 1	2	11
Scotchweld 3520	0·128	0	10 ± 1	0	12
Tra-Bond 2113	0·037	2 ± 1	9 ± 2	2	7
Tra-Bond 2114	0·024	7 ± 1	23 ± 1	6	19
Tra-Bond 2115	0·040	2 ± 1	7 ± 1	2	6
Tra-Bond 2129	0·032	4 ± 1	11 ± 6	3	8
Tra-Cast 3002	0·026	7 ± 1	25 ± 2	6	20
Tra-Cast 3010	0·038	3 ± 1	19 ± 3	2	17
Tra-Cast 3011	0·026	8 ± 1	25 ± 2	6	20
Tra-Cast 3012	0·064	25 ± 5	86 ± 20	19	69
UHU Plus	0·075	< 0·5	36 ± 1	< 1	19
UHU Plus Endfest	0·088	< 0·5	24 ± 7	< 0·5	13
UHU Plus Schnellfest	0·042	3 ± 1	13 ± 1	2	11

(1) and (2) indicate different batches.
*Dibutyl phthalate.

Table 3 Yellowing life expectancy estimates of epoxy resin adhesives (0·1mm-thick films) for various representative lighting exposure conditions found in museums

Epoxy	Life expectancy (years)					
	Unfiltered fluorescent lamp exposure (150μW/lm; 1000 lux; 22°C)		Northern window exposure (350μW/lm; 5000 lux; 22°C)		Southern window exposure (350μW/lm; 23000 lux; 22°C)	
	Slightly yellow ($A_t = 0·1$)	Strongly yellow ($A_t = 0·25$)	Slightly yellow ($A_t = 0·1$)	Strongly yellow ($A_t = 0·25$)	Slightly yellow ($A_t = 0·1$)	Strongly yellow ($A_t = 0·25$)
Ablebond 342-1	19	45	3	5	<1	<1
AR 1200	0	2	0	2	0	<1
Araldite 502/HY951	<1	2	<0·5	1	<0·5	<1
Araldite 502/HY956	2	7	<1	2	<0·5	<1
Araldite 6010/HY951	<0·5	3	<0·5	1	<0·5	<1
Araldite 6010/HY956	<0·5	3	<0·5	2	<0·5	<1
Araldite 6010/HY951 – DBP*	<1	2	<0·5	1	<0·5	<1
Araldite 6010/HY956 + DBP*	<1	2	<0·5	1	<0·5	<0·5
Araldite AW106/HV953U	<0·5	11	<0·5	4	<0·5	1
Araldite AY103/HY951	1	26	<1	14	<1	5
Araldite AY103/HY956	23	86	8	31	2	9
Armstrong A-271	2	17	2	11	1	4
Devcon EK-20	<0·5	10	<0·5	7	<0·5	6
Devcon-2-ton	3	18	<1	3	<0·5	<1
Dur-a-glaze #4	6	21	1	7	<0·5	2
EC-2216	<1	22	4	34	7	38
Eccobond 24	2	7	<0·5	2	<0·5	<1
Elmer's Epoxy	<0·5	4	<0·5	<1	<0·5	<1
Epo-Tek 301	4	15	2	12	1	7
Epo-Tek 301-1	5	27	3	17	1	7
Epo-Tek 301-2	17	48	14	40	9	24
Epo-Tek 305	1	4	<0·5	2	<0·5	1
Epo-Tek 730	<1	11	<1	5	<0·5	2
Epo-Tek 731	<0·5	7	<0·5	3	<0·5	<1
Epoweld 3672	13	48	2	7	<0·5	2
Epoxybond	<0·5	5	<0·5	1	<0·5	1
Epoxyglass	12	35	6	18	2	6
Fenwal 39-800000-918	1	5	<0·5	1	<0·5	<0·5
GAC 88 × 1250	13	38	3	8	<1	2
GAC 88 × 1295	<1	5	<0·5	2	<0·5	<1
GAC 88 × 1411	0	4	0	2	0	<1
Homalite 1100 (1)	1	90	1	13	<1	3
Homalite 1100 (2)	3	12	<1	4	<0·5	1
Homalite 1100 + DBP*	<1	5	<0·5	1	<0·5	<1
Hxtal NYL-1	59	>100	26	69	9	24
Hysol 0151	<0·5	19	<0·5	16	<0·5	11
Hysol TE6175/HD3561	5	16	3	8	<1	3
Maraglas R658/H558	5	16	3	9	1	3
PR 2400	0	5	0	<1	0	<0·5
Quik-i-poxy	2	8	<0·5	4	<0·5	1
Scotchweld 3520	0	16	0	16	0	13
Tra-Bond 2113	<1	4	<0·5	1	<0·5	<0·5
Tra-Bond 2114	3	14	<1	4	<0·5	<1
Tra-Bond 2115	1	4	<0·5	2	<0·5	<0·5
Tra-Bond 2129	2	6	<0·5	3	<0·5	<1
Tra-Cast 3002	3	13	<0·5	3	<0·5	<1
Tra-Cast 3010	2	14	<1	5	<0·5	1
Tra-Cast 3011	3	13	<0·5	4	<0·5	1
Tra-Cast 3012	11	57	3	16	<1	4
UHU Plus	<1	8	<0·5	2	<0·5	<1
UHU Plus Endfest	<0·5	4	<0·5	<0·5	<0·5	<0·5
UHU Plus Schnellfest	1	6	<0·5	5	<0·5	2

(1) and (2) indicate different batches.
*Dibutyl phthalate.

not differ significantly from estimates made under natural dark aging: the average percent reduction in life expectancy on exposure to ideal museum conditions was about 10%. For the second, third and fourth representative lighting conditions (Table 2), the average percent reductions in service life expectancy compared to natural dark aging were considerably higher—approximately 30, 60 and 75% respectively.

Table 4 The 10 epoxy formulations showing the least tendency to yellow under various representative lighting exposure conditions found in a museum (extracted from Table 3)

Exposure epoxy	*Life expectancy (years)* $A_t = 0{\cdot}1$	$A_t = 0{\cdot}25$
Dark exposure (22°C)		
Hxtal NYL-1	>100	>100
Epoweld 3672	45	>100
Araldite AY103/HY956	40	>100
Ablebond 342-1	35	>100
Tra-Cast 3012	25	86
GAC 88 × 1250	19	57
Epo-Tek 301-2	18	51
Epoxyglass	15	42
Dur-a-glaze #4	14	41
Epo-Tek 301-1	10	38
'Ideal' museum exposure (75μW/lm; 300 lux; 22°C)		
Hxtal NYL-1	>100	>100
Araldite AY103/HY956	33	100
Ablebond 342-1	27	78
Epoweld 3672	26	92
Tra-Cast 3012	19	69
Epo-Tek 301-2	17	49
GAC 88 × 1250	16	51
Epoxyglass	14	40
Dur-a-glaze #4	12	34
Epo-Tek 301-1	8	30
Unfiltered fluorescent lamp exposure (150μW/lm; 1000 lux; 22°C)		
Hxtal NYL-1	59	>100
Araldite AY103/HY956	23	86
Ablebond 342-1	19	45
Epo-Tek 301-2	17	48
Epoweld 3672	13	48
GAC 88 × 1250	13	38
Epoxyglass	12	35
Tra-Cast 3012	11	57
Dur-a-glaze #4	6	21
Epo-Tek 301-1	5	27
Northern window exposure (350μW/lm; 5000 lux; 22°C)		
Hxtal NYL-1	26	69
Epo-Tek 301-2	14	40
Araldite AY103/HY956	8	31
Epoxyglass	6	18
EC-2216	4	34
Epo-Tek 301-1	3	17
Tra-Cast 3012	3	16
Maraglas R658/H558	3	9
GAC 88 × 1250	3	8
Hysol TE6175/HD3561	3	8

Table 4 (continued)

Exposure epoxy	*Life expectancy (years)* $A_t = 0{\cdot}1$	$A_t = 0{\cdot}$
Southern window exposure (350μW/lm; 23000 lux; 22°C)		
Hxtal NYL-1	9	24
Epo-Tek 301-2	9	24
EC-2216	7	38
Araldite AY103/HY956	2	9
Epoxyglass	2	6
Epo-Tek 301-1	1	7
Epo-Tek 301	1	7
Armstrong A-271	1	4
Maraglas R658/H558	1	3
Araldite AY103/HY951	<1	5

$$A_t = [A(380\text{nm})_t - A(600\text{nm})_t] \times \frac{0{\cdot}1\text{mm}}{F}$$

where: A_t = degree of yellowing
A = absorbance
t = time
F = average film thickness for each sample.

The 10 epoxy formulations which showed the least tendency to yellow under the four representative museum conditions and dark exposure are given in Table 4. The formulations listed and their relative order are different for each exposure condition due to the nature of their yellowing curves. Five products, however, are repeated for each of the exposure conditions. These are Araldite AY103/HY956, Epo-Tek 301-1, Epo-Tek 301-2, Epoxyglass and Hxtal NYL-1. If, as is usually the case, one is uncertain as to the intensity of light to which an epoxy formulation will be exposed, one would want to choose a formulation that is the most durable under low- as well as high-intensity irradiation. The five formulations mentioned above would satisfy this requirement, with Hxtal NYL-1 and Epo-Tek 301-2 performing best overall.

4 Conclusion

In general, the results of high-intensity light aging of room-temperature-cure epoxy resin adhesives illustrated that light-induced yellowing is usually a nonlinear function of time. Since it was shown that the reciprocity principle was obeyed, the data obtained from high-intensity light aging was scaled to represent yellowing under other lower illumination levels found in a museum environment. The data treated in this way were added to the natural dark aging data, realizing, of course, the limitations of this simple approach. Service life expectancy estimates for each epoxy resin were thus determined. The results showed that the least exposure to light that epoxy resin adhesives receive, the better: exposure to direct sunlight is extremely detrimental.

Epoxy formulations Hxtal NYL-1 and Epo-Tek 301-2 appear to be the best choices when the effects of light and thermal aging are considered together. Araldite AY103/HY956, Epoxyglass and Epo-Tek 301-1 also perform relatively well.

The use of epoxy resin adhesives in situations where a repaired artifact will be subject to high-intensity light, such as in the vicinity of a window, is not advised, since all products yellowed under these conditions. In an ideal museum environment (i.e., low-intensity light exposure), the contribution of light-induced reactions to yellowing is minimal in comparison with that of thermally-induced reactions. Under the latter conditions, the service life expectancy of epoxy resins is limited only by the thermally-induced rather than by the light-induced effects and the order of selection of a suitable adhesive will be the same as for natural dark aging, as published in a previous article [2].

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Suppliers of materials

Ablebond 342-1: Conservation Materials Ltd, Box 2884, 340 Freeport Blvd, Sparks, NV 89431, USA.
AR 1200: Formulated Resins Inc., Box 508, Greenville, RI 02828, USA.
Araldite 502/HY951, Araldite 502/HY956, Araldite 6010/HY951, Araldite 6010/HY956 and Araldite AW106/HV953U: Ciba-Geigy Ltd, 205 boul. Bouchard, Dorval, Quebec, Canada H9S 1B1.
Araldite AY103/HY951 and Araldite AY103/HY956: Ciba-Geigy Ltd, Plastics Division, Duxford, Cambridge CB2 4QA, UK.
Armstrong A-271: Beacon Chemical Co. Inc., 125 Macqueston Parkway South, Mount Vernon, NY 10550, USA.
Devcon EK-20 kit and Devcon-2-ton: Devcon Canada Ltd, 22 Golden Gate Court, Scarborough, Ontario, Canada.
Dur-a-glaze #4: Dur-a-flex Inc., Box 14390, 100 Meadow Street, Hartford, CT 06114, USA.
EC-2216: 3M Canada Ltd, Box 5757, London, Ontario, Canada N6A 4T1.
Eccobond 24: Emerson and Cuming Inc., Dielectric Materials Division, Canton, MA 02021, USA.
Elmer's Epoxy 60601: The Borden Company Ltd, 1275 Lawrence Avenue East, Don Mills, Ontario, Canada M3A 1C5.
Epo-Tek 301, Epo-Tek 301-1, Epo-Tek 301-2, Epo-Tek 305, Epo-Tek 730 and Epo-Tek 731: Epoxy Technology Inc., Box 567, 14 Fortune Drive, Billerica, MA 01821, USA.
Epoweld 3672: Hardman Inc., Belleville, NJ 07109, USA.
Epoxyglass and Epoxybond: Atlas Minerals and Chemicals Inc., Farmington Road, Mertztown, PA 19539, USA.
Fenwal 39-800000-918: Fenwal Inc., Division of Walter Kidde and Co. Inc., Box 309, Ashland, MA 01721, USA.
GAC 88 × 1250, GAC 88 × 1295 and GAC 88 × 1411: General Adhesives and Chemical Co., Box 90, 6100 Centennial Blvd, Nashville, TN 37202, USA.
Homalite 1100: SGL Homalite, Division of SGL Industries Inc., 11 Brookside Drive, Wilmington, DE 19804, USA.
Hxtal NYL-1: Conservation Materials Ltd, Box 2884, 340 Freeport Blvd, Sparks, NV 89431, USA.
Hysol TE6175/HD3561 and Hysol 0151: Hysol (Canada) Ltd, 345 Finchdene Square, Scarborough, Ontario, Canada M1X 1B9.
Maraglas R658/H558: Acme Chemicals and Insulation Co., Division of Allied Products Corp., Box 1404, New Haven, CT 06505, USA.
PR 2400: Formulated Resins Inc., Box 508, Greenville, RI 02828, USA.
Quik-i-poxy L5M129: Leech Products Inc., Box 391, Fourth & Hendricks Streets, Hutchinson, KS 67501, USA.
Scotchweld 3520: 3M Canada Ltd, Box 5757, London, Ontario, Canada N6A 4T1.
Tra-Bond 2113, Tra-Bond 2114, Tra-Bond 2115, Tra-Bond 2129, Tra-Cast 3002, Tra-Cast 3010, Tra-Cast 3011 and Tra-Cast 3012: Tra-Con Inc., 55 North Street, Medford, MA 02155, USA.
UHU Plus, UHU Plus Endfest and UHU Plus Schnellfest: Lingner & Fischer GmbH Bühl, Postfach 1440, D-7580 Bühl, Baden, West Germany.

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Jane L. Down graduated from Queen's University, Kingston, Ontario, in 1973 with an Honours BSc in Chemistry and Mathematics. After working in various areas of scientific research including forensic science, biochemistry, pharmacology and pesticide chemistry, she joined the Canadian Conservation Institute in 1978. As a Conservation Scientist her main area of concern is adhesive research. *Author's address: Canadian Conservation Institute, 1030 Innes Rd, Ottawa, Ontario, Canada K1A 0M8.*

Résumé—Un certain nombre d'adhésifs aux résines époxy thermodurcissables à froid employés dans la restauration des verres ont été expérimentés quant à leur tendance au jaunissement sous une lumière de grande intensité. Les résultats ont été extrapolés à l'atmosphère des musées, prenant en compte à la fois la lumière et la contribution des conditions de température au jaunissement. On obtient pour chaque adhésif des estimations de durée de vie, c'est à dire du temps que met un film mince d'époxy à jaunir au-delà d'une limite acceptable. Bien que la majorité des produits ne conviennent pas, on a pu cependant identifier quelques formules qui avaient moins tendance à jaunir que les autres. Quelques recommandations d'usage des résines époxy sont données.

Auszug—Es wurden verschiedene, bei Raumtemperatur härtende, für Verwendung in der Glaskonservierung geeignete Epoxyharzleime auf ihre Tendenz zum Gelbwerden unter hochintensivem Licht getestet. Die Ergebnisse wurden unter Berücksichtigung sowohl licht- wie auch wärme-induzierter Beiträge zum Gelbwerden auf repräsentative Museumsbedingungen extrapoliert. Lebenserwartungsanschläge, die Zeitdauer, die ein dünner Epoxyharzfilm benötigt, um untolerierbar gelb zu werden, wurden für jeden Kleber erhalten. Obgleich die Mehrzahl der Produkte ein untolerierbares Stabilitätsniveau aufwies, wurden einige Ansätze mit weniger Tendenz zum Gelbwerden als andere identifiziert. Es werden Empfehlungen für die Benutzung spezifischer Epoxyharze gegeben.

THE YELLOWING OF EPOXY RESIN ADHESIVES: REPORT ON NATURAL DARK AGING

Jane L. Down

Abstract—Various room temperature cure epoxy resin adhesives suitable for glass conservation have been tested for their resistance to yellowing under natural dark aging conditions (22°C). Trends in yellowing in relation to chemical composition of formulations are discussed. Although the majority of epoxy resins tested demonstrated an unacceptable level of stability, some resins have been identified with an intermediate level of stability and can be recommended for use in conservation.

1 Introduction

The search for suitable adhesives for the repair and restoration of glass artifacts has in the past posed several problems [1]. Acrylic, polyester, nitrocellulose, cyanoacrylate, polyvinyl acetate, polyvinyl butyral and photo-activated formulations have been suggested as glass conservation adhesives [2]. Unfortunately, these adhesives are characterized by low polarity, resulting in inadequate bonding strengths, long setting times, severe shrinkage or chemical instability. With the advent and use of epoxy resin adhesives, many difficulties have been resolved. Room temperature cure epoxy resin adhesives are among those that satisfy most of the requirements of a good glass adhesive; in particular, they approach the high limit of polarity (high strength) [3], possess refractive indices close to those of many glasses, require no pressure for bonding and have minimal shrinkage upon curing. However, the inherent tendency for epoxy formulations to yellow with time still remains a major barrier towards their accepted use in conservation.

Studies on the yellowing of epoxy resin adhesives are few; hence, standard procedures for evaluating yellowing of these adhesives are lacking. Much of the literature deals with artificial methods of accelerating the yellowing by thermochemical and photochemical techniques. Fiorentino [2] artificially aged six commercial epoxy formulations and found one to be less yellow after aging than the others. The type of exposure and rates of yellowing were not specified.

A more thorough study on the light aging of seven epoxy resins for stained glass conservation was reported by Tennent [4]. He identified three resins that exhibited good resistance to photochemical yellowing. Evidence was also presented that dibutyl phthalate (DBP) plasticizer and alkyl phenol accelerators tended to promote photo-yellowing and that varying the component ratios altered the yellowing rates. Thermal yellowing effects were considered of little importance.

Other studies [5–16] focus more on the changes in physical and mechanical properties with aging. The relationship of these properties to yellowing has not been thoroughly explored. Industrial use of epoxies requires that they retain strength, electrical and flexural properties; colour changes are not a concern.

The identification of the mechanism of and species responsible for yellowing would be invaluable in choosing a suitable compound for use in conservation. Chemical synthesis of a superior epoxy formulation for ready availability would be ideal. At present, this ideal solution does not exist. A more practical alternative, therefore, is to identify existing commercially available epoxy products that are resistant to yellowing in the museum environment.

The discovery of a reliable method of artificially yellowing epoxy adhesives to indicate performance in a museum environment would be highly useful in assessing the resistance of epoxy formulations. Accelerated aging by thermochemical techniques has been undertaken, but problems of correlating accelerated aging with natural aging have arisen. Many formulations that appear superior by thermochemical accelerated aging techniques are not so by natural aging techniques [17]. Correlating accelerated with natural aging has proved difficult with other materials [18]. Until these difficulties can be overcome and understood, natural aging experiments still remain the best indicator of a material's performance with time because they reflect more accurately the conditions of service exposure.

The purpose of this study was to carry out natural dark aging on various commercially available room temperature cure epoxy resin adhesives in order to determine which formulations are most resistant to thermal yellowing. The contribution to yellowing by light-induced reactions will be reported separately.

2 Experimental

Seventy manufacturers were contacted and asked to

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provide samples of epoxy formulations suitable for the conservation of glass artifacts. The criteria were that the epoxy should remain clear and colourless and that the mechanical strength of the bond should remain relatively high even after 50–100 years. Although many were dubious that any epoxy would remain clear after this length of time, 24 companies participated and a total of 55 products were tested.

Each epoxy formulation was precisely weighed according to the manufacturer's specification and mixed thoroughly to ensure a homogeneous mixture. The mixed components were applied as thin films to glass slides degreased with acetone. Each formulation was allowed to cure at room temperature (22°C) for the manufacturer's recommended time. The films were allowed to sit undisturbed in the dark for seven days to ensure a complete cure before initial measurements were taken. Five replicate samples made from the same pot mixture for each formulation were prepared.

The extent of yellowing was monitored by measuring the absorption at 380 and 600nm on a Beckman Acta MVI ultraviolet-visible spectrophotometer prior to storage in the dark, at 22°C and 40–50% relative humidity.

Since yellowing is due to an increased absorption of light in the blue-purple and near ultraviolet range, film absorbance at 380nm was measured. This wavelength is the limit between the blue-purple end of the visible spectrum and the ultraviolet region. Examination of complete spectral curves for several test cases verified that degradation changes were not occurring at any other wavelengths. Absorbance at 600nm was measured to correct for any translucency, imperfections or cracking in the film and absorbance by the glass.

Samples were stored continuously in the dark, then at timed intervals (approximately six months) they were measured for absorbance at 380 and 600nm.

According to Beer's law, absorbance is directly proportional to the thickness of the sample being measured. Samples in this study were of inconsistent thickness due to the method of preparation; consequently, all absorbance data had to be standardized to a common film thickness in order for measurements to be comparable. Film thickness for the incident light area only was measured on an apparatus consisting of a Bruel & Kjaer Strain Indicator (Type 1526), a Philips displacement probe mounted on a travelling microscope with position output and an x–y recorder. The displacement versus position trace was digitized from the x–y plot using a Hewlett Packard 9874A Digitizer and 9830A programmable calculator and an average film thickness (F) for each sample was computed.

All absorbance data (A at 380 and 600nm) at timed intervals (t) were subjected to the following calculation and standardization to a film thickness of 0·1mm.

$$A_t = [A(380nm)_t - A(600nm)_t] \times \frac{0{\cdot}1mm}{F}$$

A_t represents the degree of yellowing observed at a specific time (t). Yellowing curves [plots of average A_t with time (t)] were plotted.

All epoxy formulations were analyzed by infrared spectrophotometry. Resins were cast as films on silver chloride plates and curing agents examined as thin films between sodium chloride plates. These analyses provided a basis by which the relationship between adhesive composition and yellowing could be assessed.

2.1 *Yellowing acceptability evaluation test*

Since adhesives become progressively yellow with time, it was necessary to estimate the point at which colour is perceived to be unacceptable and relate this to absorbance measurements. Accordingly, the following yellowing acceptability evaluation test was devised: 20 epoxy samples of approximately equal film thickness and of varying degrees of yellowness were selected. The 20 samples were placed on a light-table and presented to 30 persons with the following instructions:

> 'You have a clear, glass artifact that has a serious break. The pieces have been glued together with a clear epoxy. Time has elapsed and the repaired break in the artifact is turning yellow. Observe the samples of epoxy in front of you and arrange them in the following order imagining they represen. the epoxy glueline: (a) not yellow (b) tolerably yellow (c) not acceptably yellow.'

When the results were analyzed, it was found that epoxy samples with an absorbance (A_t) of less than 0·1 were always perceived as acceptable in colour while samples with absorbance (A_t) greater than 0·25 were unacceptable in colour. From 0·1 to 0·25 absorbance, uncertainty in colour acceptability existed. These limits were used as criteria to determine the approximate life expectancy of the epoxy formulations tested.

3 Results

Of the 55 formulations analyzed all but one proved to have as the resin component a diglycidyl ether of bisphenol A (DGEBA) (Figure 1). DGEBA resins can have various molecular weights. No attempt to determine the molecular weight of each commercial resin was made. The one resin formulation (Epo-Tek 305) differing from the above was composed of 1,2,3-tris(2,3-epoxypropoxy)propane (Figure 1).

Many of the resin components were found to contain fillers, plasticizers and diluents in addition to the

DGEBA resin. Chemical formulae for these additives are presented in Figure 2. The results of the individual chemical analyses of the resin components may be found in Table 1.

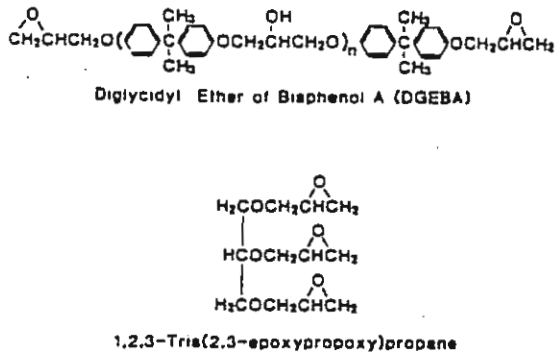

Figure 1 Chemical formulae of resin components of epoxy resin adhesives.

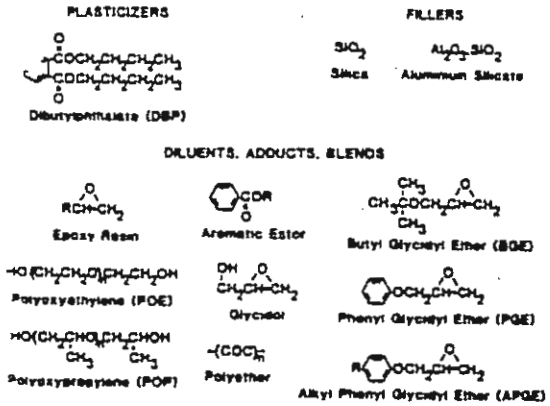

Figure 2 Chemical formulae of additives of epoxy resin adhesives.

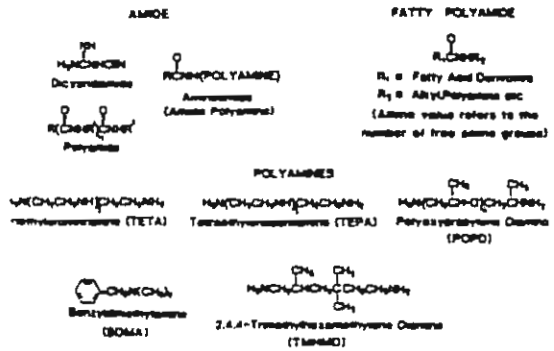

Figure 3 Chemical formulae of hardener components of epoxy resin adhesives.

Curing agents for the 55 formulations were identified as amine-containing polymers. All curing agents fell within three generalized groups: polyamines, amides and fatty polyamides. Some curing agents were found to be adducts or blends of the various groups. Chemical formulae for all curing agents are presented in Figure 3. The results of the individual analyses of the hardener components may be found in Table 1.

Yellowing curves for all products tested are presented in Figures 4 to 21. Vertical axes are absorbance (A_t: the degree of yellowing) while horizontal axes are time (t: months of elapsed time). Each point represents the data averaged from five samples. The higher the value of A_t, the more yellow the sample. Also, the steeper the slope of the curve, the greater is the rate of yellowing. The dotted horizontal lines at A_t = 0·1 and 0·25 mark off the critical range of yellowing acceptability determined from the yellowing acceptability evaluation test. The times corresponding to the intersection of the yellowing curve with the dotted horizontal lines at 0·1 and 0·25 are the limits of the life expectancy range of the epoxy. In practical terms, these are respectively the time at which a formulation will start to discolour visibly (when the yellowing curve intersects A_t = 0·1) and the time at which a formulation will appear so strongly yellowed that joint repair would be warranted (when the yellowing curve intersects A_t = 0·25). All figures represent the behaviour of a film of epoxy 0·1mm in thickness. If thicker or thinner films are considered, the data must be adjusted.

Yellowing curves presented in Figures 4 to 21 are grouped according to the chemical composition of the hardener component. In this way, similarities in the rates of yellowing for epoxies composed of the same hardener materials could be identified.

The yellowing curves were used to compile the information presented in Table 2. The life expectancy range described above was determined for each epoxy, either directly from the yellowing curve (if the yellowing curve had intersected the A_t = 0·1 or 0·25 dotted horizontal lines during the course of the experiment), or from an extrapolation of the yellowing curve to future years. The reader is forewarned that extrapolations of this nature are only estimates made on available data. Values in brackets in Table 2 indicate such extrapolations and thus reflect some uncertainty.

The comparative initial colour of each epoxy studied is given in Table 2 under the column A_0. The lower the value of A_0, the less yellow the adhesive when freshly prepared.

Feller has proposed standards of evaluation of thermoplastic resins [19]. A material that retains its desirable properties for greater than 500 or greater

Table 1 Results of chemical analysis of resin and hardener components

Hardener type	*DGEBA resin*	*Resin additives*	*Hardener additives*
Modified amine (primary amine groups, aliphatic CH_2 chains and ether linkages – no aromatics)	Epoweld 3672	—	Aliphatic amine and alkyl phenyl ether (APE)
	Maraglas R658/H558	Butyl glycidyl ether (BGE)	—
	Tra-Cast 3012	BGE	—
	Tra-Cast 3010	Polyoxypropylene (POP)	—
	Epo-Tek 310	POP	—
	Tra-Cast 3011	POP, but less than two above	—
Triethylenetetramine (TETA)	Araldite 6010/HY951	—	—
	Homalite 1100	—	—
	Araldite 502/HY951	Dibutyl phthalate (DBP)	—
	Araldite AY103/HY951	DBP	—
A mixture of TETA, tetraethylene-pentamine (TEPA) and higher polymeric ethylene amines	Araldite 6010/HY956	—	—
	Araldite 502/HY956	DBP	—
	Araldite AY103/HY956	DBP	—
Polyoxypropylene diamine (POPD)	Quik-i-poxy	—	—
	UHU Plus Schnellfest	—	—
	Lepage's 5 Minute Epoxy	Silica	Silica
2,4,4-trimethylhexamethylene diamine (TMHMDA)	Epo-Tek 301	Alkyl glycidyl ether (AGE)	—
	Epo-Tek 301-1	AGE	—
	Dur-a-glaze #4	—	Benzyldimethylamine (BMDA)
A blend or adduct of polyoxyethylene (POE) and a primary aliphatic polyamine	Hysol TE6175/HD3561	—	(Low OH)
	Eccobond 24	—	—
	Fenwal 39-800000-918	—	—
A blend or adduct of polyoxyethylene (POE) and a primary aliphatic polyamine	PR 2400 (blend)	—	—
	Epo-Tek 301-2 (adduct)	—	—
	Ablebond 342-1 (adduct)	—	—
Polyamine-epoxy resin adduct	Devcon-2-ton	—	—
	Epoxyglass	—	—
A mixture of an aliphatic polyamine and a low molecular weight aromatic ester	GAC 88 × 1295	Alkyl phenyl glycidyl ether (APGE)	—
A mixture of an aliphatic polyamine and a fatty polyamide	Epo-Tek 730	APE and aluminium silicate	Aluminium silicate: very high amine value*
	Epo-Tek 731	APE and aluminium silicate	Aluminium silicate: high amine value*
Fatty polyamide (very high amine value*)	Armstrong A-271	—	—
	AR 1200	—	—
	GAC 88 × 1411	Silica	—
Fatty polyamide (high amine value*)	Devcon EK-20	—	—
	Hysol 0151	—	—
	Araldite AW106/HV953U	DBP and silica	—
	UHU Plus	DBP and silica	—

Table 1 (continued)

Hardener type	*DGEBA resin*	*Resin additives*	*Hardener additives*
	UHU Plus Endfest	DBP and silica	—
	Elmer's Epoxy 60601	Silica	2,4,6-tris (dimethylaminomethyl) phenol (DMP-30) and silica
	Araldite AV100/ HV100	Silica	DMP-30 and silica
	Araldite RP103/ HY991	DBP	—
Fatty polyamide (low amine value*)	Renweld RP106	DBP	—
	Lepage's 354	Silica	—
	Lepage's Epoxy	Silica	—
Fatty polyamide adducted or blended with POE	Scotchweld 3520	—	(High amine value*)
	EC-2216	—	(Low amine value*)
Amino-amide adducted with phenyl glycidyl ether (PGE)—no free epoxide	Canus 1000/68	—	—
	Tra-Bond 2129	BGE	—
	Tra-Bond 2113	BGE	(High amino-amide content)
POE blended or adducted with a lyamide/epoxy adduct	Tra-Bond 2115	—	—
	Tra-Cast 3002	BGE	—
	Tra-Bond 2114	BGE	—
POP blended or adducted with dicyandiamide	GAC 88 × 1250	APGE	—
Unidentified	Epoxybond	Silica and silicate	—
Hardener type	*1,2,3-tris (2,3-epoxy propoxy) propane resin*	*Resin additives*	*Hardener additives*
TMHMDA	Epo-Tek 305	—	—

*Amine value of a fatty polyamide refers to a measure of the reactive function per gram of resin.

than 100 years (Class A1 and A2 respectively) is an excellent conservation material. One that degrades in 20 to 100 years (Class B) has an intermediate ranking. A product that degrades in less that 20 years (Class C) is considered an unstable product, whereas one that degrades in less than six months (Class T) should only be considered a temporary conservation material. Based on this stability classification, epoxy formulations tested are presented in Table 2 in order of the most resistant to yellowing to the least resistant adhesive.

4 Discussion

The results of natural dark aging illustrate that the natural yellowing process of epoxy resin adhesives is not a linear function of time. Many of the yellowing curves resemble the type of deterioration curve discussed first by Grassie in 1956 [20], and then by [illegible]er in 1977 [21]: that is, a non-linear curve characterized by three distinct stages. The first stage, an induction period, is indicative of little or no yellowing—the initial portion of the yellowing curve has a slope of almost zero. Several of the yellowing curves presented in Figures 4 to 21 display this induction period. In cases where this feature is missing, the induction period may occur so quickly that it fails to be detected by the first measurement of absorbance. The second stage is a steady state period. During this time, the rate of yellowing is high and relatively constant—the yellowing curve displays a steep and straight slope. The final stage is the declining rate stage. This is the phase in which an increase in yellowing is occurring, but at a slower rate than the steady state phase—the late portion of the yellowing curve, with a more gently increasing slope, illustrates this state.

The results presented in Figures 4 to 21 suggest that these three stages occur in most of the yellowing curves, but at different times. Predicting life expectancy of an epoxy formulation is most accurate if its yellowing curve has progressed to the declining rate stage. Ideally, epoxy resins should be monitored for

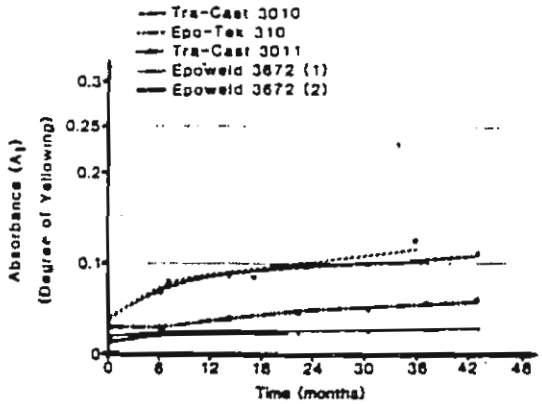

Figure 4 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and modified amine hardeners on yellowing.

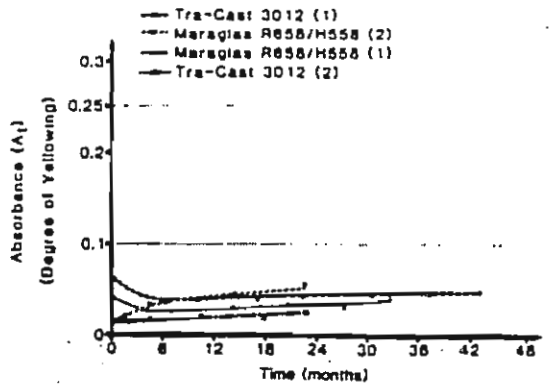

Figure 5 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and modified amine hardeners on yellowing.

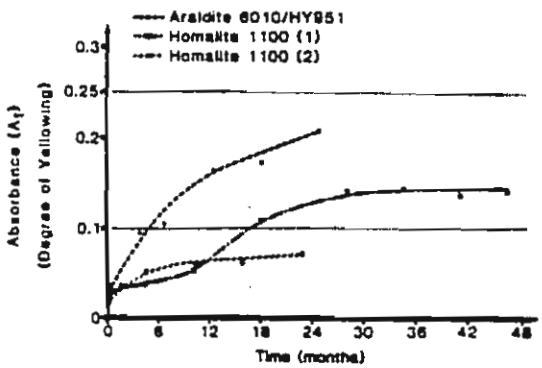

Figure 6 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and TETA hardeners on yellowing.

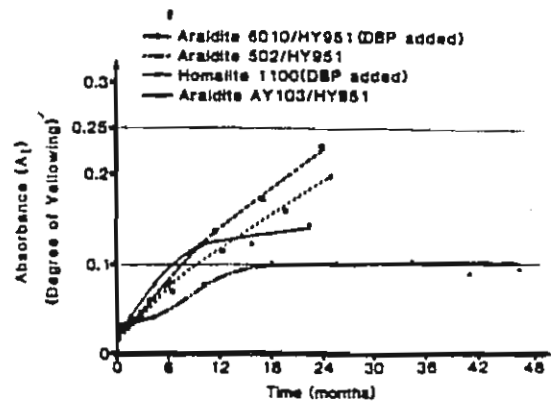

Figure 7 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins containing DBP plasticizer and TETA hardeners on yellowing.

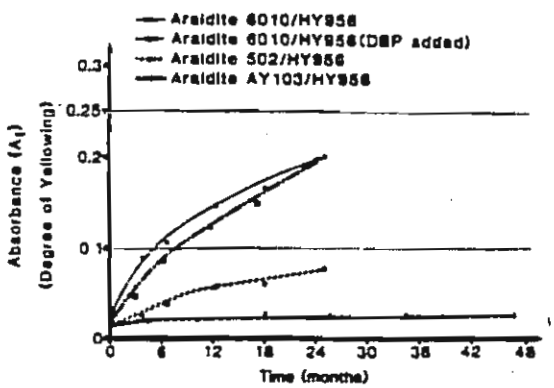

Figure 8 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and hardeners composed of a mixture of TETA, TEPA and higher polymeric ethylene amines on yellowing.

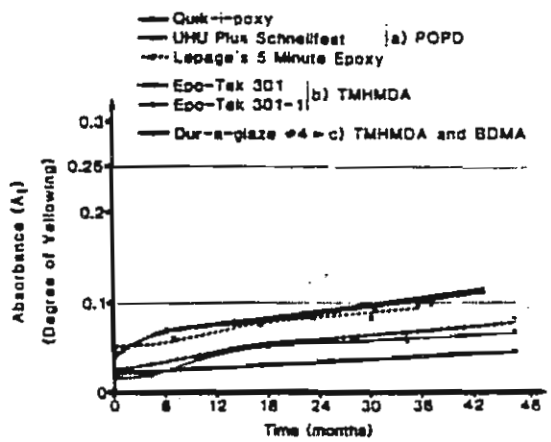

Figure 9 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and (a) POPD hardeners, (b) TMHMDA hardeners, (c) a hardener composed of a mixture of TMHMDA and BDMA on yellowing.

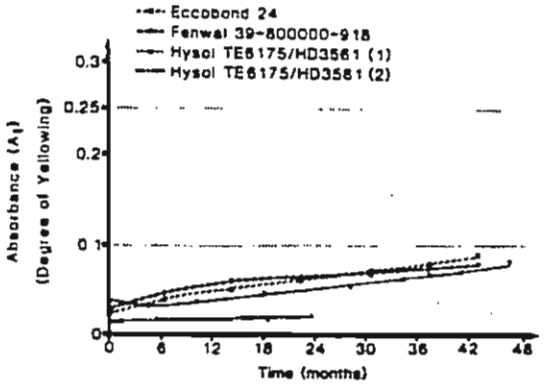

Figure 10 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and hardeners composed of a blend or adduct of POE and a primary aliphatic polyamine on yellowing.

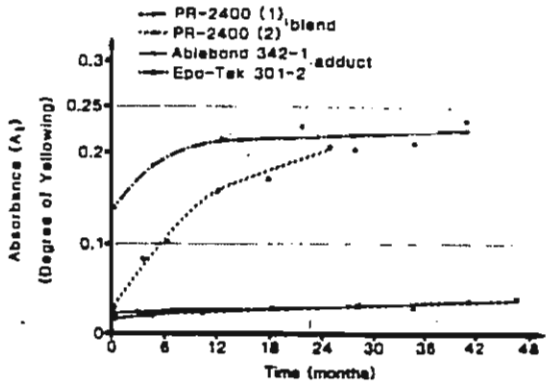

Figure 11 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and hardeners composed of a blend or adduct of POP and an aliphatic polyamine on yellowing.

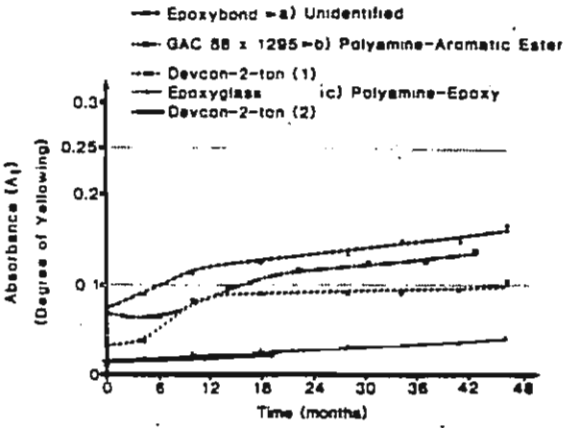

Figure 12 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and (a) an unidentified hardener, (b) a hardener composed of a mixture of an aliphatic polyamine and a low molecular weight aromatic ester, (c) polyamine-epoxy resin adducted hardeners on yellowing.

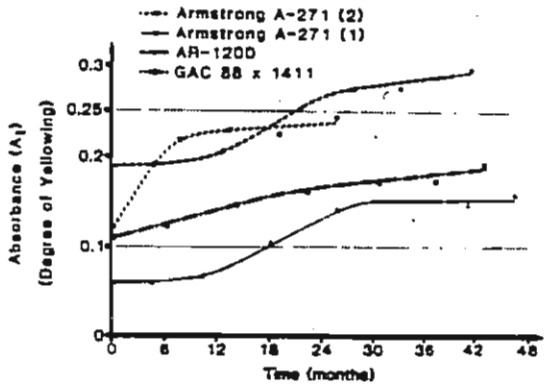

Figure 13 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and fatty polyamide (very high amine value) hardeners on yellowing.

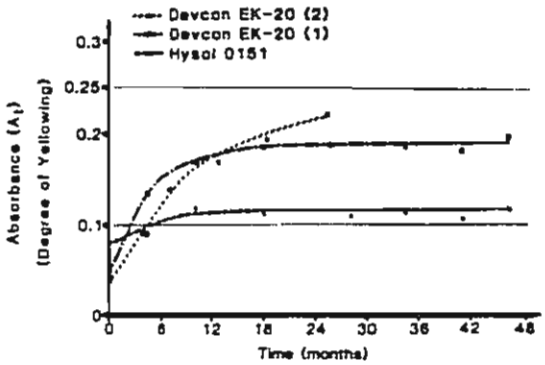

Figure 14 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and fatty polyamide (high amine value) hardeners on yellowing.

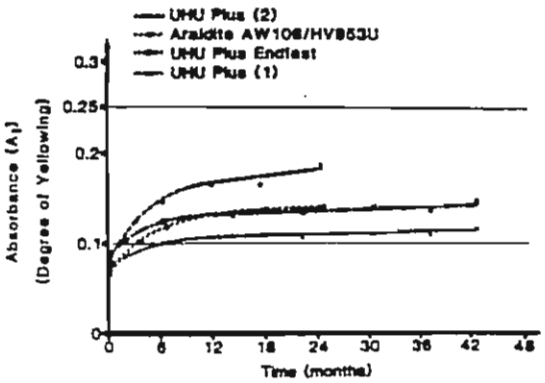

Figure 15 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins containing DBP plasticizer and silica and fatty polyamide (high amine value) hardeners on yellowing.

Table 2 *Life expectancy range of various epoxy resin adhesives of 0·1mm thickness under natural dark aging (22°C)*

Stability class*	Epoxy	Initial colour (A_0)	Life expectancy range (years ± standard deviation)	
			Slightly yellow (A_t = 0·1)	Strongly yellow (A_t = 0·25)
Class B	Epoweld 3672 (1) [3·6]	0·018	(45 ± 11)	(>100 ± 34)A2
	Araldite AY103/HY956 [3·9]	0·016	(40 ± 7)	(>100 ± 21)A2
	Ablebond 342-1 [1·2]	0·022	(35 ± 19)	(>100 ± 54)A2
	Tra-Cast 3012 (1) [3·6]	0·064	(25 ± 5)	(86 ± 20)
	Epoweld 3672 (2) [1·8]	0·008	(23 ± 2)	(65 ± 7)
	Hysol TE6175/HD3561 (2) [2·0]	0·013	(23 ± 5)	(63 ± 14)
Class C	GAC 88 × 1250 [3·6]	0·022	(19 ± 3)	(57 ± 8)
	Tra-Cast 3012 (2) [1·9]	0·017	(19 ± 4)	(54 ± 11)
	Epo-Tek 301-2 [3·9]	0·017	(18 ± 5)	(51 ± 13)
	Maraglas R658/H558 (1) [2·7]	0·041	(16 ± 5)	(46 ± 15)
	Epoxyglass [3·9]	0·012	(15 ± 2)	(42 ± 7)
	Dur-a-glaze#4 [3·9]	0·021	(14 ± 2)	(41 ± 7)
	Devcon-2-ton (2) [1·6]	0·013	(12 ± 1)	(33 ± 2)
	Epo-Tek 301-1 [3·9]	0·018	(10 ± 4)	(38 ± 15)
	Fenwal 39-800000-918 [3·6]	0·028	(9 ± 2)	(38 ± 10)
	Epo-Tek 301 [3·9]	0·025	(8 ± 3)	(27 ± 13)
	Tra-Cast 3011 [3·6]	0·026	(8 ± 1)	(25 ± 2)
	Tra-Cast 3002 [3·6]	0·026	(7 ± 1)	(25 ± 2)
	Tra-Bond 2114 [3·6]	0·025	(7 ± 1)	(23 ± 1)
	Maraglas R658/H558 (2) [1·9]	0·016	(6 ± 1)	(18 ± 3)
	Hysol TE6175/HD3561 (1) [3·9]	0·039	(6 ± 1)	(17 ± 2)
	Homalite 1100 (2) [1·9]	0·021	(5 ± 1)	(17 ± 2)
	Eccobond 24 [3·6]	0·023	(5 ± 1)	(14 ± 1)
	Devcon-2-ton (1) [3·9]	0·029	4 ± 1	(26 ± 5)B
	Lepage's 5 Min. Epoxy [3·0]	0·052	4 ± 1	(17 ± 4)
	Tra-Bond 2129 [3·6]	0·032	4 ± 1	(11 ± 6)
	Tra-Cast 3010 [3·6]	0·038	3 ± 1	(19 ± 3)
	UHU Plus Schnellfest [3·6]	0·042	3 ± 1	(13 ± 1)
	Quik-i-poxy [3·6]	0·041	3 ± 1	(12 ± 1)
	Araldite 502/HY956 [2·1]	0·016	(3 ± 1)	(9 ± 1)
	Homalite 1100 (1) [3·9]	0·030	2 ± 1	(>100)A2
	Renweld RP106 [3·0]	0·071	2 ± 1	(26 ± 9)B
	Amstrong A-271 (1) [3·9]	0·056	2 ± 1	(19 ± 9)
	Epo-Tek 310 [3·0]	0·037	2 ± 1	(10 ± 1)
	Tra-Bond 2113 [3·6]	0·037	2 ± 1	(9 ± 2)
	Epo-Tek 305 [3·9]	0·031	2 ± 1	(9 ± 1)
	Tra-Bond 2115 [3·6]	0·040	2 ± 1	(7 ± 1)
	Canus 1000/68 (1) [3·0]	0·028	2 ± 1	(7 ± 3)
	Araldite AY103/HY951 [3·9]	0·031	1 ± 1	(36 ± 11)B
	GAC 88 × 1295 [3·6]	0·068	1 ± 1	(13 ± 1)
	Araldite RP103/HY991 [3·0]	0·071	1 ± 1	(13 ± 4)
	EC-2216 [3·9]	0·081	<1	(20 ± 3)B
	Epoxybond [3·9]	0·077	<1	(12 ± 5)
	Epo-Tek 730 [3·9]	0·075	<1	(11 ± 2)
	Homalite 1100 + DBP [1·9]	0·022	<1	(8 ± 3)

Table 2 (continued)

Stability class	Epoxy	Initial colour (A_0)	Life expectancy range (years ± standard deviation)	
			Slightly yellow (A_t = 0·1)	Strongly yellow (A_t = 0·25)
	Araldite 502/HY951 [2·1]	0·018	<1	(3 ± 1)
	Araldite 6010/HY956 + DBP [2·0]	0·020	<1	(3 ± 1)
	Araldite 6010/HY951 + DBP [2·0]	0·017	<1	2 ± 1
Class T	UHU Plus (1) [3·6]	0·075	<0·5	(36 ± 11)B
	UHU Plus Endfest [3·6]	0·088	<0·5	(24 ± 7)B
	Araldite AW106/HV953U [2·1]	0·068	<0·5	(20 ± 7)
	Hysol 0151 [3·9]	0·080	<0·5	(19 ± 3)
	Devcon EK-20 (1) [3·9]	0·049	<0·5	(13 ± 5)
	Epo-Tek 731 [3·9]	0·083	<0·5	(8 ± 1)
	Lepage's Epoxy [3·0]	0·079	<0·5	(7 ± 2)
	Elmer's Epoxy [3·9]	0·094	<0·5	(7 ± 1)
	UHU Plus (2) [2·0]	0·083	<0·5	(5 ± 1)
	PR 2400 (2) [2·0]	0·029	<0·5	(4 ± 2)
	Devcon EK-20 (2) [2·1]	0·039	<0·5	(3 ± 1)
	Araldite 6010/HY956 [2·1]	0·019	<0·5	(3 ± 1)
	Araldite 6010/HY951 [2·1]	0·024	<0·5	(3 ± 1)
	Canus 1000/68 (2) [1·6]	0·029	<0·5	(2 ± 1)
	Scotchweld 3520 [3·9]	0·128	0	(10 ± 1)
	PR 2400 (1) [3·4]	0·140	0	(8 ± 2)
	GAC 88 × 1411 [3·6]	0·106	0	(7 ± 1)
	Lepage's 354 [3·0]	0·123	0	(6 ± 1)
	Armstrong A-271 (2) [2·2]	0·120	0	(3 ± 1)
	AR 1200 [3·4]	0·188	0	2 ± 1
	Araldite AV100/HV100 [3·0]	0·187	0	1 ± 1

[A]Standards of intended use of materials in conservation [19]: Class A1 = excellent (>500yrs), Class A2 = excellent (>100yrs), Class B = intermediate (20–100yrs), Class C = unstable (<20yrs), Class T = temporary (<6mo.).

(1) and (2) indicate different batches. Values in square brackets indicate the number of years of natural dark aging that the specific adhesive has undergone.

yellowing until the final stage is evident. Frequently, however, adhesive selection is based on a single before and after aging measurement with the assumption that yellowing occurs in a linear manner. This approach can sometimes furnish misleading information as can be illustrated with the yellowing curves in Figures 15 and 16. At six months, Araldite RP103/HY991 epoxy films (A_{6mo} = 0·078; induction state) were less yellow than UHU Plus (1) films (A_{6mo} = 0·101; declining rate stage). If one assumed linearity of the yellowing curves and ceased to monitor the films beyond six months, the selection of Araldite RP103/HY991 as the adhesive more resistant to yellowing would be made. Continued monitoring of the films, however, demonstrated that after two years, UHU Plus (1) films (A_{2yrs} = 0·111; declining rate stage) were, in fact, less yellow than Araldite RP103/HY991 (A_{2yrs} = 0·135; declining rate stage). This was because the yellowing curves were not linear and the declining rate stages of the two adhesives began at different times. It is important, therefore, to monitor epoxy films undergoing natural aging at frequent intervals and continue until such time as the declining rate stage is evident. In some situations, the degree of yellowing of a product may become unacceptable before its yellowing curve has reached the declining rate stage. It would not be necessary to continue monitoring such a product since it has already reached a level of unacceptable colour.

Some of the yellowing curves for epoxy products tested in this study had not, at publication, progressed to a declining rate stage or reached an unacceptable degree of yellowing. Life expectancy estimates made on such products and listed in Table 2 are bracketed, reflecting the uncertainty of the estimate.

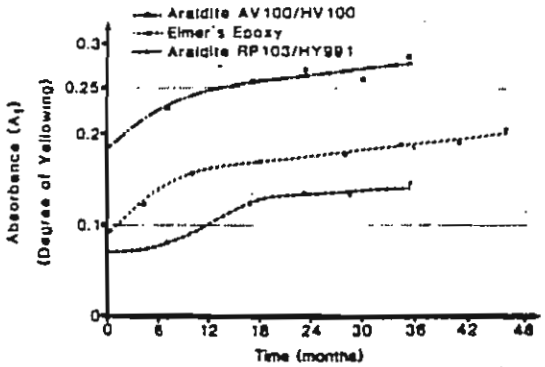

Figure 16 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins containing various additives and fatty polyamide (high amine value) hardeners on yellowing.

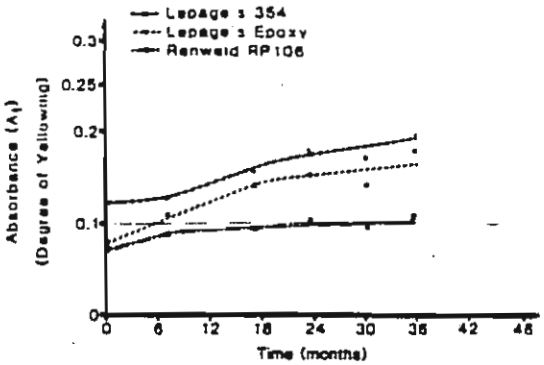

Figure 17 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and fatty polyamide (low amine value) hardeners on yellowing.

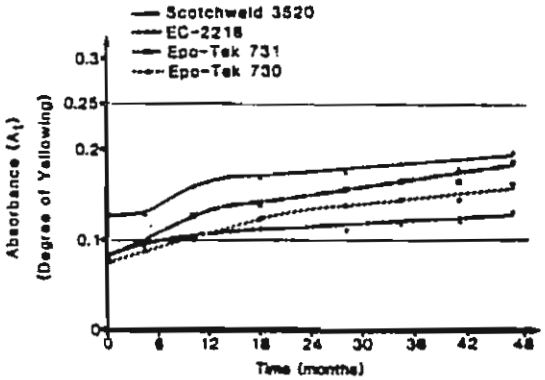

Figure 18 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and fatty polyamide adducted or blended hardeners on yellowing.

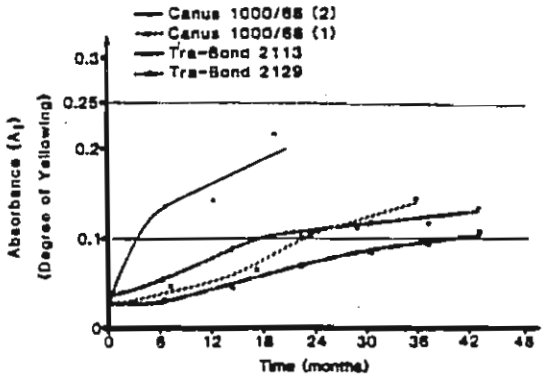

Figure 19 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and amino-amide·PGE adducted hardeners on yellowing.

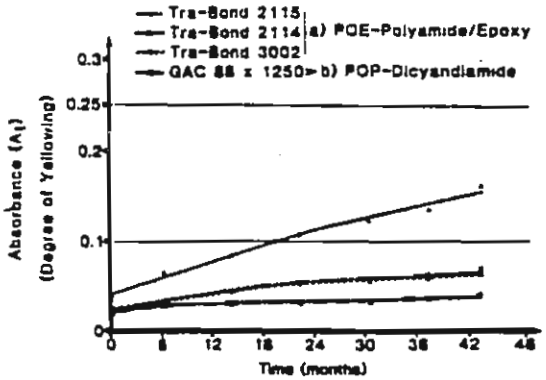

Figure 20 The effect of natural dark aging of epoxy resin adhesives with DGEBA resins and (a) hardeners composed of POE blended or adducted with a polyamide/epoxy adduct, (b) a POE-dicyandiamide blended or adducted hardener on yellowing.

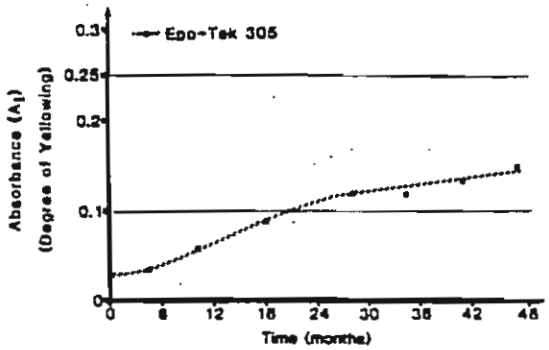

Figure 21 The effect of natural dark aging of epoxy resin adhesives with 1,2,3-tris(2,3-epoxypropoxy)propane resin and a TMHMDA hardener on yellowing.

Monitoring of these formulations is continuing and will be reported in future communications as warranted.

Some general trends and similarities in the rates of natural yellowing presented in Figures 4 to 21 for each epoxy hardener group will now be discussed.

4.1 Modified amine hardener (Figures 4 and 5)
Epoxy resin adhesives containing this hardener tended to have good initial colour. In general, the rates of yellowing were relatively slow. Systems containing polyoxypropylene (POP) diluent in the resin had faster steady state rates than those which did not have POP. Most formulations containing butyl glycidyl ether (BGE) diluent in the resin displayed an initial induction period of bleaching. Yellowing curves of formulations containing BGE had not progressed, at publication, to a declining rate stage. Formulations containing BGE and an alkyl phenyl ether (APE) had long life expectancies.

2 Triethylenetetramine (TETA) hardener or a rdener mixture of TETA with tetraethylenepentamine (TEPA) and higher polymeric ethylene amines (Figures 6–8)
These adhesives tended to have good initial colour. For the most part, steady state rates of yellowing were very fast while declining rates were relatively slow. A consistent trend in the yellowing behaviour of adhesives containing DBP plasticizer did not emerge. In general, life expectancies for this group of adhesives were short.

4.3 Polyoxypropylene diamine (POPD) hardener (Figure 9)
Adhesives with this hardener tended to have moderately good to poor initial colour. In general, the rates of yellowing were moderately fast and life expectancies were short.

4.4 Trimethylhexamethylene diamine (TMHMDA) hardener (Figure 9)
Formulations containing this hardener displayed good initial colour. The rates of yellowing tended to be slow, with the systems containing alkyl glycidyl ether (AGE) diluent in the resin showing slightly faster steady state rates than ones with benzyldimethylamine (BDMA) adducted to the hardener. Life expectancies were relatively long.

4.5 A blend or adduct of polyoxyethylene (POE) th a primary aliphatic polyamine hardener (Figure 10)
Adhesives containing this hardener tended to have good initial colour. In general, the rates of yellowing were slow and life expectancies were relatively long.

4.6 An adduct of POP with an aliphatic polyamine hardener (Figure 11)
Epoxy resins containing this hardener were inclined to have good initial colour. Rates of yellowing tended to be slow, resulting in long life expectancies for this group of adhesives.

4.7 A blend of POP with an aliphatic polyamine hardener (Figure 11)
These adhesives displayed inconsistencies in their initial colour. One batch had good initial clarity while the other had a poor initial colour. Both batches, however, displayed very fast steady state rates of yellowing and very short life expectancies.

4.8 Polyamine-epoxy resin adducted hardener (Figure 12)
This group of adhesives tended to have good initial colour. Rates of yellowing were generally slow except for one formulation (Devcon-2-ton) which displayed a very fast steady state rate. Life expectancies for this group were relatively long.

4.9 Fatty polyamide hardener (Figures 13–18)
Formulations containing this type of hardener displayed poor initial colour. Some of these adhesives tended to exhibit long, slow induction periods; however, most steady state rates were very fast. Although declining rates were relatively slow, life expectancies for this group were very short.

4.10 An adduct of phenyl glycidyl ether (PGE) with an amino-amide hardener (Figure 19)
Epoxy resin adhesives containing this hardener displayed good initial colour. Steady state rates, in general, were moderate to fast while life expectancies tended to be short.

4.11 A blend or adduct of POE with a polyamide/epoxy adduct hardener (Figure 20)
This group of adhesives tended to have good initial colour. The rates of yellowing were inclined to be moderately slow. Adhesives containing BGE diluent in the resin had slower rates and longer life expectancies that those adhesives with no BGE present.

4.12 A blend or adduct of POP with dicyandiamide hardener (Figure 20)
This formulation had good initial colour. Rates of yellowing were slow, yielding a long life expectancy.

In some cases, two separate batches of the same product were tested as new samples were received. These are distinguished in the figures and Table 2 by (1) and (2) following the product name. Often life expectancy estimates for the two batches differed, even though the bulk of the two products were identified by infrared spectrophotometry to be com-

posed of the same polymers. These differences can be attributed mainly to trace impurities which were not identified. In addition, more data, and hence a more complete and reliable yellowing curve, were available for the first batch. Although the numerical estimates of lifetime in these cases differ considerably, the classification into Feller's categories of stability usually remains the same.

The majority of epoxy formulations tested fell into Class C (unstable) or Class T (temporary) as defined by Feller's stability classification (Table 2). Epoweld 3762, Araldite AY103/HY956, Ablebond 342-1 and Tra-Cast 3012 were the most stable adhesives tested, although they possessed only an intermediate level of stability against the first onset of visible discoloration. Ranking next in order of stability, but classified as unstable, were adhesives GAC 88 × 1250, Epo-Tek 301–2, Epoxyglass and Hysol TE6175/HD3561. The stability classification was determined for thin films of 0·1mm thickness. Thicker films would appear yellower and have shorter life expectancies while thinner, clearer films would have longer life expectancies. However, the order of selection of the epoxies given in Table 2 remains the same irrespective of film thickness.

5 Conclusion

The results of natural dark aging show that the thermal component of yellowing of room temperature cure epoxy resin adhesives is a non-linear function of time. Yellowing curves are characterized by two or three distinct rate stages. Since these stages occur at different times depending on the epoxy, it is important to monitor the yellowing of these products until the final stage is evident or until the degree of yellowing becomes unacceptable.

Correlation of the composition of the epoxy formulations with natural dark aging results was done so that predictions of stability of untested products could be made. Based on an average ranking of products with a common hardener, the slowest rates of yellowing and longest life expectancies were demonstrated by compositions with a DGEBA resin and hardeners of the following types: an adduct of POP with an aliphatic polyamine, blends or adducts of POP with dicyandiamide, modified amines, trimethylhexamethylene diamine, blends or adducts of POE with a primary aliphatic polyamine and a polyamine-epoxy resin adduct. Formulations containing fatty polyamides are inadequate for conservation purposes because of their poor initial colour and fast rates of yellowing.

Although the majority of products tested possessed an unacceptable level of stability as films of 0·1mm, Epoweld 3672, Araldite AY103/HY956, Ablebond 342–1 and Tra-Cast 3012 were identified with an intermediate level of stability against yellowing under natural dark aging.

Acknowledgements

The author wishes to thank Raymond H. Lafontaine, Chief of Environment and Deterioration Research, for his expert guidance and advice during the course of the project. Also many thanks to Elizabeth Moffatt and Scott Williams of Analytical Research Services for carrying out the analyses of the epoxy formulations. A special thanks is expressed to all the companies who submitted samples for inclusion in the study.

Suppliers of materials

Ablebond 342–1: Conservation Materials Ltd, Box 2884, 340 Freeport Blvd, Sparks, NV 89431, USA.

AR 1200: Formulated Resins Inc., Box 508, Greenville, RI 02828, USA.

Araldite 502/HY951, Araldite 502/HY956, Araldite 6010/HY951, Araldite 6010/HY956 and Araldite AW106/HV953U: Ciba-Geigy Ltd, 205 boul. Bouchard, Dorval, Quebec, Canada H9S 1B1.

Araldite RP103/HY991: Plastics Maritime Ltd, PO Box 1375, Halifax, NS, Canada.

Araldite AY103/HY951, Araldite AY103/HY956 and Araldite AV100/HV100: Ciba-Geigy Ltd, Plastics Division, Duxford, Cambridge CB2 4OA, UK.

Armstrong A-271: Beacon Chemical Co. Inc., 125 MacQueston Parkway South, Mount Vernon, NY 10550, USA.

Canus 1000/68: Canus Plastics Ltd, 340 Gladstone Avenue, Ottawa, Ontario, Canada K2P 0Y8.

Devcon EK-20 kit and Devcon-2-ton: Devcon Canada Ltd, 22 Golden Gate Court, Scarborough, Ontario, Canada.

Dur-a-glaze #4: Dur-a-flex Inc., Box 14390, 100 Meadow Street, Hartford, CT 06114, USA.

EC-2216: 3M Canada Ltd, Box 5757, London, Ontario, Canada N6A 4T1.

Eccobond 24: Emerson & Cuming Inc., Dielectric Materials Division, Canton, MA 02021, USA.

Elmer's Epoxy 60601: The Borden Company Ltd, 1275 Lawrence Avenue East, Don Mills, Ontario, Canada M3A 1C4.

Epo-Tek 301, Epo-Tek 301–1, Epo-Tek 301–2, Epo-Tek 305, Epo-Tek 310, Epo-Tek 730, and Epo-Tek 731: Epoxy Technology Inc., Box 567, 14 Fortune Drive, Billerica, MA 01821, USA.

Epoweld 3672: Hardman Inc., Belleville, NJ 07109, USA.

Epoxyglass and Epoxybond: Atlas Minerals & Chemicals Inc., Farmington Road, Mertztown, PA 19539, USA.

Fenwal 39–800000–918: Fenwal Inc., division of Walter Kidde & Co. Inc., Box 309, Ashland, MA 01721, USA.

GAC 88 × 1250, GAC 88 × 1295 and GAC 88 × 1411: General Adhesives & Chemical Co., Box 90, 6100 Centennial Blvd, Nashville, TN 37202, USA.

Homalite 1100: SGL Homalite, a division of SGL Indus-

tries Inc., 11 Brookside Drive, Wilmington, DE 19804, USA.

Hysol TE6175/HD3561 and Hysol 0151: Hysol (Canada) Ltd, 345 Finchdene Square, Scarborough, Ontario, Canada M1X 1B9.

Lepage's 5 Minute Epoxy, Lepage's Epoxy and Lepage's 354: Lepages Ltd, 50 West Drive, Bramlea, Ontario, Canada L6T 2J4.

Maraglas R658/H558: Acme Chemicals & Insulation Co., division of Allied Products Corp., Box 1404, New Haven, CT 06505, USA.

PR 2400: Formulated Resins Inc., Box 508, Greenville, RI 02828, USA.

Quik-i-poxy L5M129: Leech Products Inc., Box 391, Fourth & Hendricks Streets, Hutchinson, KS 67501, USA.

Renweld RP106: Ren Plastics, a Ciba-Geigy company, 5656 South Cedar, Lansing, MI 48909, USA.

Scotchweld 3520: 3M Canada Ltd, Box 5757, London, Ontario, Canada N6A 4T1.

Tra-Bond 2113, Tra-Bond 2114, Tra-Bond 2115, Tra-Bond 2129, Tra-Cast 3002, Tra-Cast 3010, Tra-Cast 3011 and Tra-Cast 3012: Tra-Con Inc., 55 North Street, Medford, MA 02155, USA.

UHU Plus, UHU Plus Endfest and UHU Plus Schnellfest: Lingner & Fischer GmbH Bühl, Postfach 1440, 7580 Bühl, Baden, West Germany.

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2 Fiorentino, P., and Vlad Borrelli, L., 'A preliminary note on the use of adhesives and fillers in the restoration of ancient materials with special reference to glass', *Studies in Conservation* 20 (1975) 201–205.

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Jane L. Down graduated from Queen's University, Kingston, Ontario in 1973 with an Honours BSc in Chemistry and Mathematics. After working in various areas of science including forensic science, biochemistry, pharmacology and pesticide chemistry, she joined the Canadian Conservation Institute in 1978. As a Conservation Scientist her main area of concern is adhesive research. *Author's address: Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario, Canada K1A 0M8.*

Résumé—On a comparé la résistance au jaunissement sous vieillissement naturel à l'abri de la lumière (22°C), de différentes résines époxy durcissables à la température ambiante et susceptibles d'être utilisées pour la restauration des verres. Les tendances au jaunissement ont été étudiées en relation avec les formulations chimiques. Bien que la plupart des résines époxy essayées se soient averées inutilisables du point de vue de leur stabilité, certaines se sont révélé d'un niveau de stabilité acceptable et peuvent être recommandées en restauration.

Auszug—Es wurden verschiedene, bei Zimmertemperatur aushärtende, für die Glaskonservierung geeignete Epoxyharzklebstoffe auf ihre Beständigkeit gegen Gelbwerden unter natürlicher Dunkelalterung (22°C) getestet. Es werden die Tendenzen zum Gelbwerden in Relation zur chemischen Zusammensetzung von Ansätzen erörtert. Obgleich die Mehrzahl der getesteten Epoxyharze ein unannehmbares Stabilitätsniveau aufwiesen, wurden einige Harze mit einem Zwischen-Stabilitätsniveau identifiziert und können zur Verwendung in der Konservierung empfohlen werden.

GLASS AND ENAMEL CONSERVATION

Collected papers from a one-day meeting on The Conservation of Glass and Enamels held on 11 November 1989.

Editor: Christine Daintith

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THE CONSERVATION OF STAINED GLASS

Peter Gibson

Abstract
A summary of conservation procedures is followed by a description of the conservation of the fire damaged Rose Window of York Minster after the fire of 9th July 1984.

The need for conservation

The actual factors that determine whether or not a stained glass window requires conservation include the condition of the lead[1], the deterioration of the glass[2] and often the condition of the *ferramenta*, the iron window bars used to support painted glass panels. The leading may be buckled or broken, particularly along the soldered joints, and partially corroded on the interior. The glass itself may be dull, pitted or crusted, and show evidence of moss growth or algae. The painted line-work may be loose, or there may be missing areas. Previous conservation work such as overpainting or misordering of the design must be noted. The condition of the *ferramenta* may be good, or may be broken or rusted, the rusted parts affecting surrounding stonework due to volume increase during corrosion. This paper will concentrate on the conservation of stained glass as carried out by the York Glaziers Trust. Space does not permit a full discussion of re-leading techniques and the refixing of panels *in situ*.

Photography in situ

Any stained glass which is to undergo conservation, whatever its date, should always be photographed *in situ* by the conservator before any work is undertaken. Black and white prints, colour prints and colour transparencies should be taken of the whole window and of individual panels. Any special corrosion or damage should be taken in close-up. Not only the glass should be photographed but also the surrounding stonework and mullions if they are also in need of attention. Ideally the inspection of the glass by the conservator should take place with both the custodian/owner of the glass and the architect responsible for the fabric of the building present.

Pre-conservation report

The report by the conservator should include comments on the condition of the lead and of the glass, and condition of the stonework in relation to any problem associated with the removal of the glass. Itemized estimated costings for all aspects of the work to be carried out should be included. The report should also state the likely timetable for the conservation work.

Conservation procedures[3]

A decision must be made as to whether the restoration work can be carried out *in situ* or whether the window must be removed. *In situ* conservation work will require ladders, portable scaffolding or specialist scaffolding.

Removal of a stained glass window

When the stained glass is removed from its location it is desirable that the architect responsible for the fabric of the building be present. This enables the architect to see the condition of the stonework and to assess whether or not there is any need for remedial work to be carried out on the stonework. It is first necessary to ensure that none of the glass is so loose in its leading that it might fall out. If it is loose temporary reversible support must be provided. Fablon is used for this purpose. It is a transparent, protective, auto-adhesive covering which is affixed to the external surface of the glass, and not to the internal painted surface. In the case of a single crack, Scotch masking tape may be used on the unpainted surface.

A plan of the window, with measurements and numbering of the individual panels, should be made and the numbers scratched onto the appropriate part of the leading. (The Corpus Vitrearum system for the numbering of panels may be used, or the conservator's own system of numbering). There are various ways of fixing windows into stonework and therefore the fixing method must be identified in order to remove the window with the least risk of damage to the window or to the surrounding stonework. As the glass is freed of surrounding mortar templates can be taken of any shaped stonework and tracery, before proceeding to the removal of the panels[4]. A temporary filling will have been agreed upon for the window space and the templates will ensure that the replacement window is a correct fit. Templates will also be of use in the workshop, during repair work.

Once the glass is safely removed to the Conservation Workshop it should be examined on an illuminated glass table. If photographs are available from a previous inspection or restoration note should be made of any differences in weathering. Any lead or copper ties should be unsoldered so that they do not damage an adjacent panel during storage. Areas of loose paint should be noted, and dust removed with a soft brush. The panel should be photographed once again before any work is undertaken.

A stained glass conservator should have access to an art historian who can be consulted about any problems relating to the iconography of the panel and he/she should have the opportunity to inspect the panel before it is dismantled. Before the panel is dismantled a tracing (called a 'rubbing') is taken of the lead outline of the panel. This is carried out by placing over the panel white detail paper and rubbing through the paper with brown or black cobbler's heel ball in order to mark the position of every lead in the panel. The exact shape of each piece of glass will be recorded on the rubbing, which is then laid on a wooden bench and covered with a sheet of glass larger than the panel; 3mm thick glass for smaller panels but 6mm for larger. The dismantling of the panel is carried out by cutting the lead cames and soldered joints with a sharp knife and then extracting the individual pieces of glass and placing them on their appropriate positions on the rubbing. Great care must be exercised in the dismantling

operation to prevent damage or cracking of the glass. If medieval lead is encountered it should be preserved.

Cleaning procedures

Loose paintwork can be reattached before cleaning is carried out. The York Glaziers Trust prefers not to intervene at the original paint layer, but protects deteriorating paintwork by the plating process described below. Water is usually regarded as a safe method of cleaning, but it is potentially damaging if any paintwork is weak. A weak solution of Synperonic non-ionic detergent in water has been recommended [5].The York Glaziers Trust use three main cleaning methods for glass:

The ultra-sonic bath

This method involves the use of an ultra-sonic generator and a small tank in which there is a dilute solution of ammonium hydroxide. (5 parts water to I part ammonium hydroxide). Twenty or thirty pieces of glass can be treated at a time. Scientific tests [6] under the guidance of Professor R G Newton, former Honorary Scientific Advisor to the Trust and also a Trustee, indicated that a three minute immersion period was acceptable provided the painted details of the glass were stable. However, enamelled glass should not be cleaned in the ultra-sonic bath.

Glass fibre brushes

If the painted detail on the surface of the glass is not secure then the glass should be cleaned manually with hand-held glass fibre brushes, using a binocular microscope in order to avoid damage to the glass. Glass fibre brushes are effective in removing hard weathering crusts in a small area at a time. This method is more time consuming and must be taken into account in the estimated costings.

Airbrasive equipment[7]

If the glass is so pitted and corroded that it will not respond to either the ultra-sonic cleaning or cleaning with glass fibre brushes then the Trust feel justified in recommending to the client, as a last resort, the use of the airbrasive equipment. There are, however, critics of this very drastic method of cleaning medieval glass and the permission of the client and any other bodies concerned should be obtained. A variety of abrasives ranging from very hard silicon carbide to very soft sodium bicarbonate can be used. Painted details on the glass may be protected by a covering of latex to ensure that no damage is caused to the paint. It is emphasised that the Trust only use this method of cleaning if no other type of cleaning has proved effective.

Chemical cleaning methods

Chemical cleaning methods such as the use of ethylenediaminetetracetic acid (EDTA) must be carefully monitored and the process arrested as soon as the last traces of weathering crust have been removed. The solution becomes more alkaline as the cleaning proceeds and this is damaging to the glass. Calgon and other sequestrants should not be used, as they will remove ions from the glass. The use of strong alkalis (and to a lesser extent acids) will affect the silica lattice.

Reglazing procedures

Once the glass has been cleaned and if any movement or alteration to the positioning of the individual pieces of glass is proposed then art historical advice must be sought by the conservator. A decision must be made as to whether to conserve the window in its present form or to restore it in the spirit of the original style. The latter choice may involve the painting of missing areas either directly onto the medieval glass or onto a backing plate and advice and permission for such restoration work must be sought. The re-assembly of the glass and the glazing takes place in the Trust workshop on perspex-topped benches that are pierced with holes to accommodate the glazing nails that are required to keep the glazing secure on the bench.

When carrying out conservation work on York Minster glass where individual pieces of original glass are missing the Trust have access to a 'bank' of medieval and later glass. This consists of about 7,000 individual pieces of glass that have been removed from misplaced positions in York Minster windows over a period of many years. If no suitable piece of glass can be found in the bank then nineteenth century or modern replacement glass is used.

Repair of broken glass

Broken pieces of glass are edge-joined with a silicone mastic adhesive, Dow Corning Silicone Sealant, which, after application to the edges of the cracked glass and with sufficient time allowed for curing, has the important advantage of remaining flexible for a considerable period of time. The joined pieces are then plated, a process which involves the sandwiching of the repaired glass between two pieces of identically shaped clear float glass of 3-4mm thickness, and the treble thickness is then sealed at the edge with a mastic strip or silicone rubber and held in an extra-wide lead. Re-leading is then carried out [8].

Waterproofing

A panel reglazed with ancient glass is made waterproof by manually inserting a butyl mastic between the flange of the lead came and the restored glass. A butyl rubber sealing strip such as Scotchseal 5313 (3M) may also be used. The strip will stick to both the glass and the lead and absorb any movement between them, remaining flexible for a considerable number of years.

Protection from weathering agents

Various methods have been used and are being used for the protection of medieval and also later glass[9]. They include the use of plate glass, perspex or polycarbonate and wire guards, none of which are totally desirable, although they all provide a degree of protection. External

glazing which mirrors the leadwork pattern of the stained glass may be carried out, and has been used at York and Canterbury. Isothermal protective glazing has been used on the Continent for many years, and in recent times has been introduced in English churches, for example, at Fairford and Gloucester. Aesthetic, scientific and practical considerations should be taken into account when installing protective glazing[10].

Conservation records

Once the panel has been completed and made waterproof then conservation records are taken of glass restored by the Trust. This entails the recording of both written and photographic details. The Royal Commission on Historical Monuments (England) have the opportunity to take photographs of glass restored by the Trust both for their own records and the National Monuments Records Office. Conservation records are also a requirement by the Council for the Care of Churches and a proportion of any grant money which enabled the work to be carried out is not paid to the conservator until the submission of completed conservation records. If the restored glass has attracted the interest of art-historians linked with Corpus Vitrearum then, provided it meets with the approval of the client, they also have the opportunity to photograph and record the glass.

Conclusion

No stained glass conservator should feel isolated when undertaking any conservation project. There is sufficient art historical, technical and scientific expertise available for sound advice to be obtained on any problem associated with the care of stained glass[11]. The main consideration should always be the preservation of the glass and the aim should be to ensure that the magnificent treasures of medieval glass that are our inheritance in the twentieth century can be enjoyed by countless future generations.

Case study: The conservation of the fire damaged Rose Window of York Minster

The conservation of the fire damaged Rose Window of York Minster presented the York Glaziers Trust with an unprecedented challenge to restore the multi-cracked glass to its former beauty. The sixteenth century glass painted by Flemish craftsmen was cracked into 40,000 pieces in the Minster fire of 9th July 1984. The three weeks immediately following the fire were crucial because as the glass cooled added tensions were set up in the glass and more cracking occurred. Temporary scaffolding was erected against the window, which was examined six times per day for three weeks. Regular examination ensured that as glass became loose and detached from the lead cames it could be gently eased back into the lead.

Temporary support

Once the main scaffolding had been erected internally and externally it was possible for a transparent adhesive

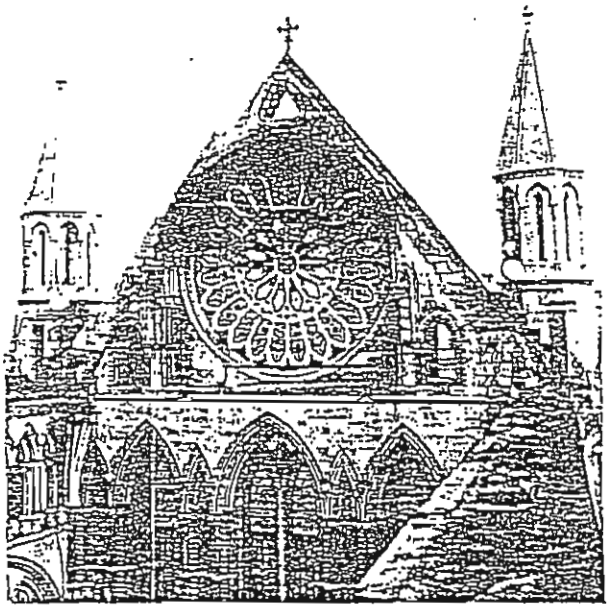

Fig. 1 The damaged South Transept of York Minster after the fire of 9 July 1984. The early 16th century stained glass of the Rose Window survived the fire although cracked into 40,000 pieces.

covering to be put on the external surface of the multi-cracked glass. The material used was Fablon, which was applied by gently pressing into position. The purpose of this was to prevent pieces of glass becoming detached during the loosening of the mortar-cement, which caused vibration of the panel and also of the multi-cracked glass. All the seventy-three panels were removed from the window and were safely stored in the Trust Workshop.

Repair of the glass and choice of adhesive

Normal conservation procedure by the Trust when repairing cracked glass is to edge-join the broken pieces together using a silicone adhesive. To gain access to the edges of the glass the panels are dismantled. However, the multi-cracked condition of the Rose Window meant that the cracked glass had to be repaired before the panels were dismantled for releading.

Twenty pieces of glass of different colours and various degrees of cracking were extracted from the damaged panels. These samples were examined by Dr Norman Tennent, at that time Chief Conservation Scientist at the Glasgow Museum and Art Gallery and Professor R G Newton, Honorary Scientific Adviser to the Trust, so that a suitable adhesive could be selected. The main properties that are required in an adhesive for stained glass are:

a. good ageing properties;
b. low surface tension;
c. a refractive index to match that of the glass[12].

Ablebond 342.1, a low viscosity two-part epoxy resin, was selected.

Conservation procedures

The fire damaged panels were first photographed and then a rubbing of the lead cames was made before cleaning of the fire-stained glass. Removal of the fire-staining proved extremely difficult and a very mild com-

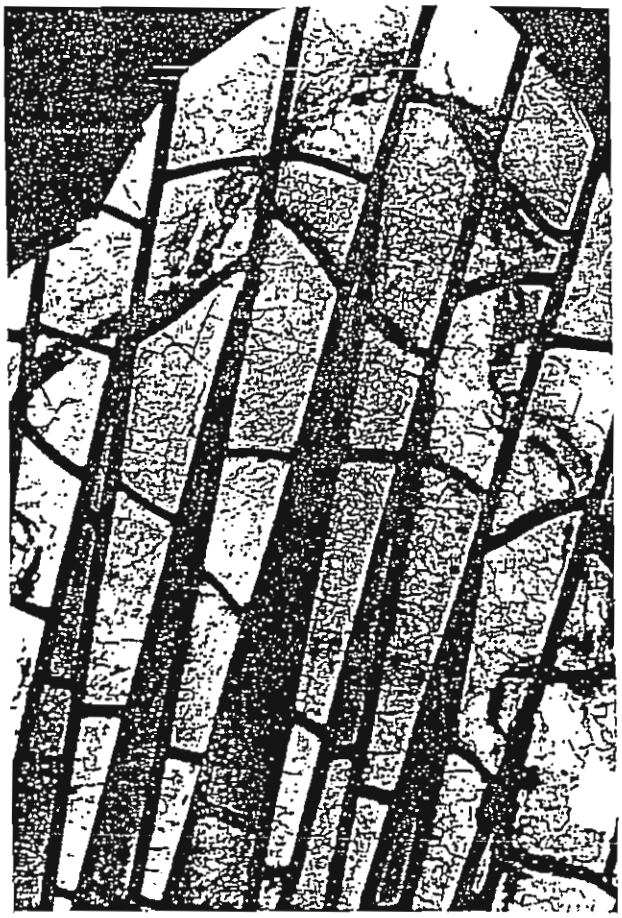

Fig. 2 A fire-cracked section of the Rose Window.

mercial detergent had to be used. This was applied with soft cloths and was removed with industrial methylated spirits.

The Ablebond 342.1 two-part epoxy resin was weighed to exact proportions on a scientific balance and then injected into the cracks and fissures by means of a pipette. Capillary action ensured a speedy penetration of adhesive into the cracks within minutes, following which any surplus adhesive was cleaned from the surface of the glass with acetone. The panels then stood undisturbed for one week to allow the adhesive to cure. They were then dismantled, the pieces of multi-cracked glass which formed the mainpart now being held securely together. Each repaired piece of glass was placed in its appropriate position on the rubbing. Dichloromethane was used to remove excess cured resin and then the Fablon on the external surface of the glass was removed and the surface of the glass cleaned using acetone.

Plating

The multi-cracked glass was then plated, using 3-4 mm clear float glass, and silicone adhesive was used to cover the edges of the treble thickness of glass. Any pieces of ancient glass that had two or three cracks only were secured together with adhesive and protected externally with a single piece of clear glass, and edge sealed with silicone adhesive. Any damaged modern glass that was inserted during the previous 1968 - 1970 restoration was not repaired but simply replaced with modern glass.

Re-leading

During the re-leading of the panels the treble thickness of glass was accommodated in the leadcames by using lead of an increased depth and the re-glazing of the panels took place on illuminated perspex benches.

Re-insertion of the repaired glass

By March 1987 the work was completed. The panels were mortar pointed in position and the external scaffolding dismantled. This splendid Tudor glass now shines in its restored glory high in the gable of the South Transept, a lasting tribute to the work of the Flemish glass painters who created the window centuries ago and a testimony to the conservation skills of the twentieth century.

Health and Safety

When using equipment or chemicals mentioned in this paper COSHH regulations should be followed. Particular note should be made of the following materials:

Ablebond 342.1: Uncured epoxy resins can cause irritation or sensitization due to contamination of the skin or eyes by the liquid or solid uncured material or by exposure to its vapour or dust. Toxic effects can occur through ingestion or absorption through the skin. Respiratory irritation can be caused by dust from the machining of fully cured material.

Do not allow uncured epoxy material to come into contact with the eyes or skin, and wear gloves, overalls and eye protection, and nose and mouth protection when there is risk of dust. Cover any skin abrasions to eliminate the possibility of accidental contact with the material.

Acetone, Industrial methylated spirits: Avoid sources of ignition and moderate skin contact.

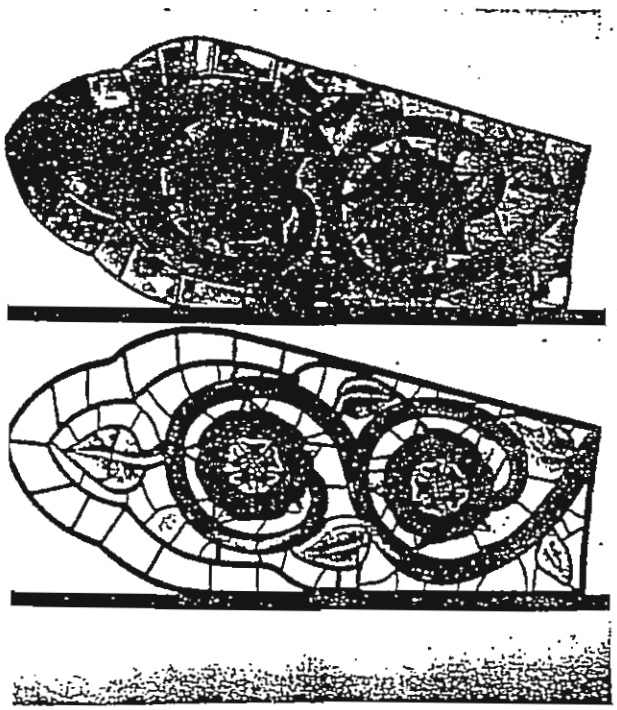

Fig. 3. Rose Window panels before and after conservation.

Airbrasive equipment: Some abrasive powders may contain free silica or other potentially hazardous ingredients. Gloves and the appropriate mask should be worn when filling the mixing chamber.

mmonium hydroxide: Strong solutions of ammonia are caustic. They liberate pungent toxic ammonia gas and inhalation must be avoided. Work in a fume cupboard or wear appropriate protective equipment.

Dichloromethane: Burns and degreases skin on contact, and can cause eye damage. Work in a fume cupboard wearing rubber (nitrile) gloves.

Ethylenediaminetetracetic acid (EDTA): May be harmful by ingestion, inhalation or skin absorption. Wear gloves, goggles and a respirator, or work in a fume cupboard.

Glass fibre brushes: Gloves and a dust mask should be worn and waste material disposed of in a container.

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Addresses

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9 Montague Close
London Bridge
London SEI 9DD

Council for the Care of Churches
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London EC2M 5NA

Suppliers

Airbrasive equipment: GEC-Elliot Mechanical Handling Ltd, Birch Walk, Erith, Kent DA8 1QH.

Butyl-mastic: Adshead Ratcliffe & Co, Belper, Derby DE51 XYJ.

Float glass: Pilkington Glass Ltd., Prescot Road, St Helens, Merseyside WA10 3TT.

Modern 'antique' glass : Hartley Wood & Co., Monkwearmouth, Sunderland, Tyne and Wear SR6 ODN.

Silicone Adhesive/Sealants : Hansil Ltd., Wintersells Road, Byfleet, Surrey KT14 7LH.

Ultra-Sonic equipment : L R Ultrasonics, I5 Claremont Road, Wealdstone, Harrow, Middlesex HA3 7AX.

Window lead : Heaps, Arnold & Heaps Ltd, Leeds Lead Works, Clarence Road, Leeds, LS10 1UB.

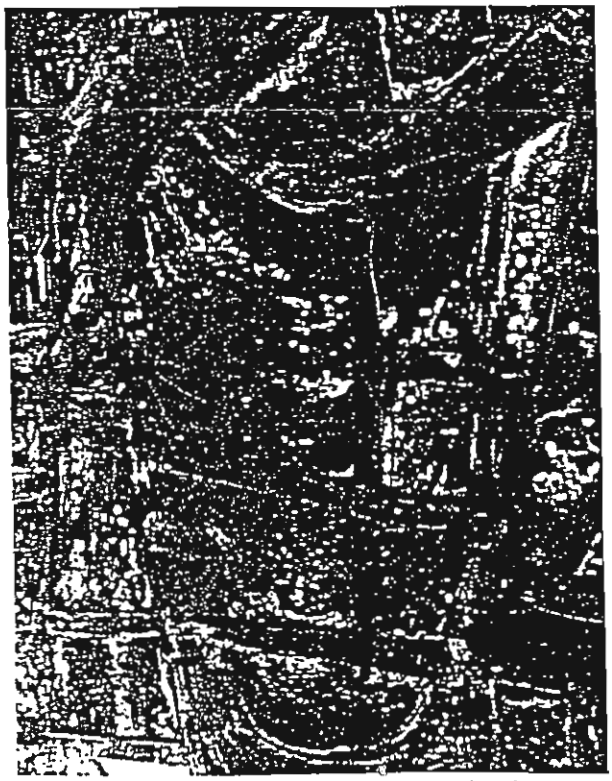

Fig.4 Stained glass of York Minster c1320 showing external pitting and corrosion of glass due to weathering.

GLASS RECONSTRUCTION MATERIALS AND TECHNIQUES

Colin Brain

Abstract
This paper discusses the selection of adhesives and fill materials for glass reconstruction, including the use of density as a means of inferring refractive index, and techniques for using these materials to replace missing portions of transparent vessel glasses. The results achieved are discussed and priorities for improvement suggested.

Introduction

The transparency and brittleness of glass have made it highly valued through the ages. In 1586 in his 'Description of England' Harrison wrote: *'It is a world to see in these our daies, wherin gold and silver most aboundeth, how that our gentilitie as loathing those mettals (because of the plentie) do now generallie choose rather the Venice glasses...'*[1] However it is just these valued qualities which cause the special problems associated with glass conservation and demand the kind of materials and techniques outlined here. The study of glass, its archaeology, its history and its conservation seems imprecise compared with ceramics and consequently approaches to glass conservation appear individualistic and dependent on the background and training of the conservator. The paper has been divided into two parts, materials and techniques, even though the two are interdependent.

Materials

There are three characteristics of finished materials which are of prime importance in glass conservation; these are all related to the influence the material has on light. These characteristics are; refractive index (RI) which influences the refraction of light, colour and clarity which alter light transmission, and surface finish which affects the reflection of light. The latter is mainly technique dependent and will be touched on later. The importance of RI matching, particularly with adhesives, has been amply demonstrated in the past, e.g. by Norman Tennant and Joyce Townsend[2]. The main problem facing the conservator with limited equipment is the determination of the RI of the glass to be repaired. A technique which can be adopted uses the relationships between the density of typical glasses and their RI which can be derived from standard reference sources[3]. This technique was the subject of a short note in Conservation News[4] and it has since been found that this approach has a long pedigree[5]. Fig 1 shows graphs of the variation of RI with density for flint (lead) and crown glasses (for a simple technique of determining density see appendix 1). From this it can be seen that there is a good correlation for flint glass, which is not surprising in view of the fact that both the RI and the density depend on the lead content of the glass. The figure also shows a range of adhesives used in glass conservation and it can be seen that these allow a fair match across much of the range. The correlation for crown glasses is not as good, which is only to be expected given the more diverse range of glass compositions.

RI matching obtained using this technique has proved excellent, but it is ironic that the best example of its effectiveness was in one case when it was not used. This was a repair of a broken knop in the stem of a wine glass. The fractures were such that the only way it could be

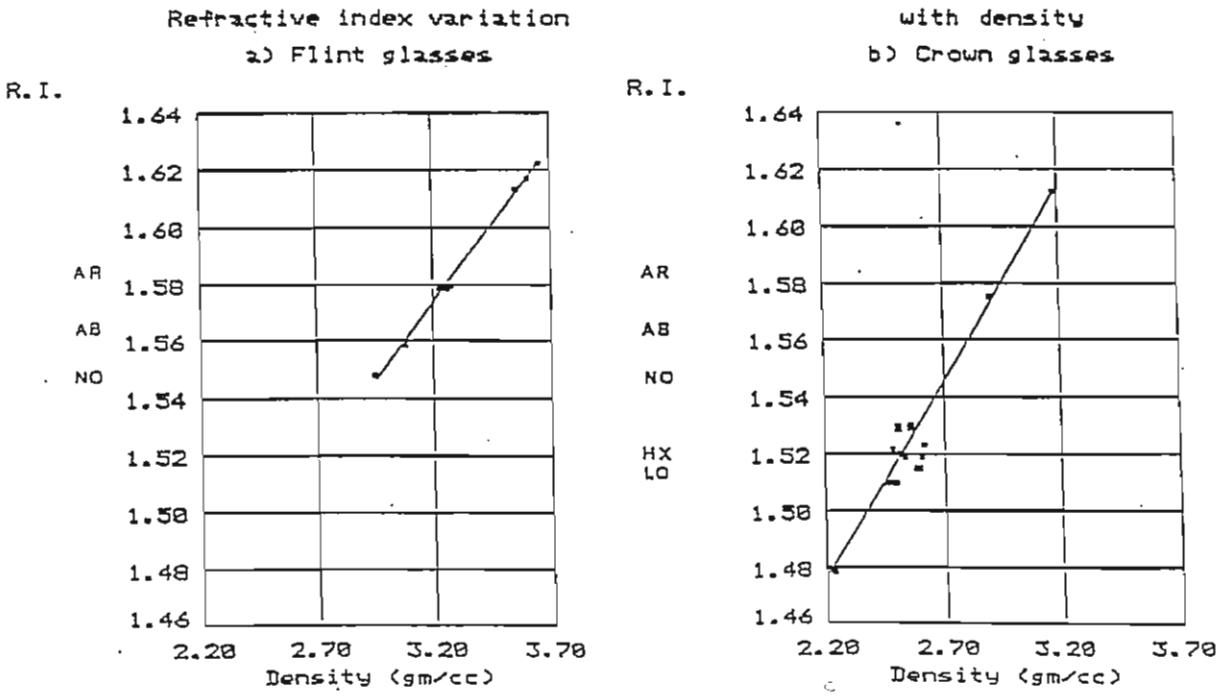

Fig.1 Showing relationship between glass refractive index and density (AR - Araldite AY105/HY951, AB - Ablebond 342-

Fig.2 17th century decanter jug requiring restoration.

repaired was by using a UV-curing adhesive, holding the pieces in place manually during the short cure. That being the case, no attempt was made to match the RI. When the repair was complete, it proved virtually invisible. Since the match was so good, the density of the glass was measured and this coincided almost exactly on the graph with the reported RI for the adhesive used, Loctite Glassbond. In most cases it should be fairly obvious whether a glass belongs to the flint or crown glass category, but in cases of doubt its fluorescence under ultra-violet light should be conclusive; flint glass fluoresces blue, whilst non-flint glass usually shows yellow. When using UV light in this way, UV eye protection should be used to prevent any risk of eye damage.

The next aspect is that of adhesive and filling material colour changes due to ageing. There have been a number of papers covering this point, but these have usually employed artificial ageing techniques in order to achieve in weeks what would normally take years. These published studies did not cover exactly the same materials and techniques used by the author and this led to a concern as to the representativeness of such techniques. Consequently in January 1987 it was decided to undertake a natural ageing test in the workshop. The procedure used was simple: mixing a little excess material; curing this in the pot; cutting the resultant disc in half; labelling the halves and putting one half in a box in a drawer to dark age, and the other between the panes of a south-facing double-glazed window. In order to record the progress of the ageing, colour photographs of the sample pairs were taken at intervals, including a stable colour reference in the picture. Although the procedure lacks sophistication, it is easy and effective and will be continued as a routine quality control check. The materials tested and the results achieved by this technique were reported in an earlier note[6].

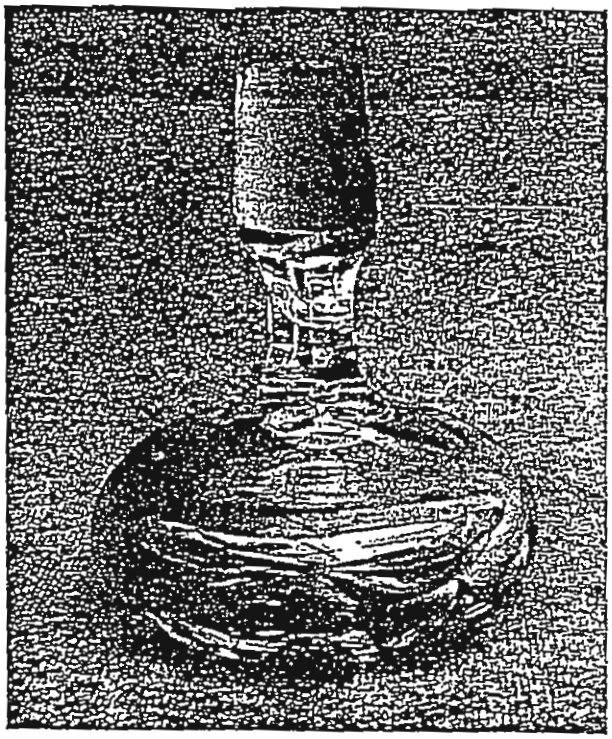

Fig.3 Restored decanter stopper.

Techniques

The techniques which will be briefly covered are those used to replace missing portions of bowls or feet of vessel glasses. Before starting this kind of work it is necessary to consider whether the value of doing the work outweighs the cost of doing it. This is not easy since 'value' must be considered in a broad context and cost must include the effect on the glass of any irreversible actions, in addition to the cost of the conservator's work. The latter may be simply the time, materials, etc., involved, or it may be a matter of a lost opportunity to undertake other conservation work. When considering the value of a particular course of action it must be remembered that a glass, say a seventeenth century English wine glass, needs to be considered in three different historical contexts. The industrial archaeologist considers it as a product of the seventeenth century glass industry in England, the social historian sees it as part of the development of drinking utensils in seventeenth century England, and the art historian sees it as an example of the applied arts of that period. The conservator also needs to consider whether the work can be undertaken to the required standard and whether the original form of the vessel being reconstructed can be established with confidence. There is an unfortunate paradox here; often a piece for which reconstruction is most desirable is one for which the original shape is least certain. For example, if there are ten complete examples which are similar to a vessel being reconstructed, there should be little doubt over its original form, but correspondingly how much value is there in providing another apparently complete example? Conversely if no comparable pieces are known, there may be some doubt concerning the original form, but an inexact reconstruction might still be of considerable value. Thus there is a need for either considerable background knowledge, or expert advice in deciding the best course of action. Unfortunately in the case of glass this knowledge or advice is not always easy to obtain. The author has found it necessary to build up a data base of

information on English seventeenth century drinking glass from excavated material and published references; approximately a thousand of these glasses have been catalogued, providing a valuable reference source.

As discussed earlier, one of the key issues with filling is surface finish. The use of dental wax, to form a mould round a missing section, is an effective technique which will be familiar to many readers, but whilst it is invaluable in some applications it is incapable of achieving surface finishes of a quality comparable to many glasses. This can then lead to the use of abrasives in an attempt to rectify the situation and these can cause serious damage to the glass. Another aspect of this technique is that it is difficult to make a second attempt if the colour match is not ideal. An alternative technique is to make a replacement segment for a bowl by casting a clear or coloured resin sheet of the correct thickness on a polished flat glass surface, allowing this to partially cure, trimming it roughly to shape, wrapping this around a core turned to fit the internal bowl profile, and completing the cure in this position. The core can be made of any convenient material, for example wood or plaster-of-Paris. The process of fitting the edges of the new segments to the old is then tedious, but this is helped by marking the cut line on the core. If this technique is used where all of the bowl rim is missing, it leaves a problem join up one side of the bowl. In this case a better method is to make the segment by casting resin onto a core which is the shape of the inside of the bowl, and then machining the outside of the resin bowl to the correct profile. A good external finish can be achieved in this way.

The success of this technique is partly dependant on the release agents used. Wax and polytetrafluoroethane (PTFE) release agents have been used with limited success, but none has proved totally satisfactory.

When the whole of a bowl rim of a vessel is missing, there is obviously some doubt as to the original size of the bowl. There are a number of clues which can be used to estimate this size. One of these is the ratio of the bowl rim diameter to the foot rim diameter, since this is often fairly constant across a range of glasses. Another pointer is the taper of the bowl wall thickness. If this is fairly linear it will give a maximum height where the rim thickness would taper to zero (assuming the taper is towards the rim, which is not always the case). Often bowl capacities fall into certain groups, depending on the use for which they were designed, and this may be helpful. Finally the fracture dynamics of bowls often follow set patterns, provided the glass is reasonably homogeneous, and this may also be used to infer the position of the rim. Where these different clues give similar estimates of rim position, this may be used with some confidence, but where the estimates conflict there is a need to carefully reconsider the ethical questions raised earlier.

Plaster-of-Paris has been used to form moulds of more complex shapes, such as the foot of a glass. Care must be taken not to constrain the material on drying, since this can cause stresses due to expansion. In order to do this a wax release agent is applied to the intact part of the foot, opposite to the area to be filled (since glass vessel feet are often elliptical rather than round) and the foot is placed on waxed paper. Plaster-of-Paris is then applied to the top surface of the foot. When this is dry, the foot plus mould is peeled off the paper and the part of the mould which was in contact with the paper is sealed with a cellulose sealant and treated with wax release agent. The foot is then inverted, and plaster-of-Paris applied to form the other half of the mould. When both halves have been removed from the foot, they are sealed, treated with a wax release agent and rejoined to form a moulding cavity. Silicone rubber is used by many restorers in preference to plaster-of-Paris, particularly for complex shapes. The most difficult task of this type is to replace part of a non-symmetrical vessel; adequate means of dealing with this which will produce the desirable quality of surface finish are lacking.

Conclusion

This paper has briefly covered some aspects of material selection and some of the techniques used for employing these materials to replace missing portions of vessel glasses. These techniques work well in some cases, but in others, such as the non-symmetrical case mentioned, they are not ideal and there is still a long way to go before there can be any sense of complacency in this field. Of the many aspects requiring further study, two in particular may be singled out. The first is the question of how close a match it is worth seeking between the refractive indices of the glass and adhesive and the second is how an accurate colour match for both reflected and transmitted light can be reliably achieved?

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Appendix 1

Procedure for the determination of glass density

1. Weigh fragment of glass and record weight (W_a grams).
2. Repeat (1) with the fragment suspended on a thread and completely immersed in water (W_w).
3. The weight of water displaced by the fragment is then W_a minus W_w.
4. The volume of fragment (V) is then (W_a - W_w) divided by the density of water p (p is approximately 1 gram per cubic centimetre for water).
5. If the fragment contains an air bubble, the volume (V) should be corrected by subtracting the approximate volume of the bubble (in cubic centimetres).
6. The density of the glass is then Wa divided by V (gm/cc).

Note. This procedure must be modified if a pan balance is used. Instead of step 2, weigh a container full of water on the pan and then note the increase in this weight when the fragment is suspended on a thread in the water. This increase is the weight of water displaced by the fragment, which is required for step 3.

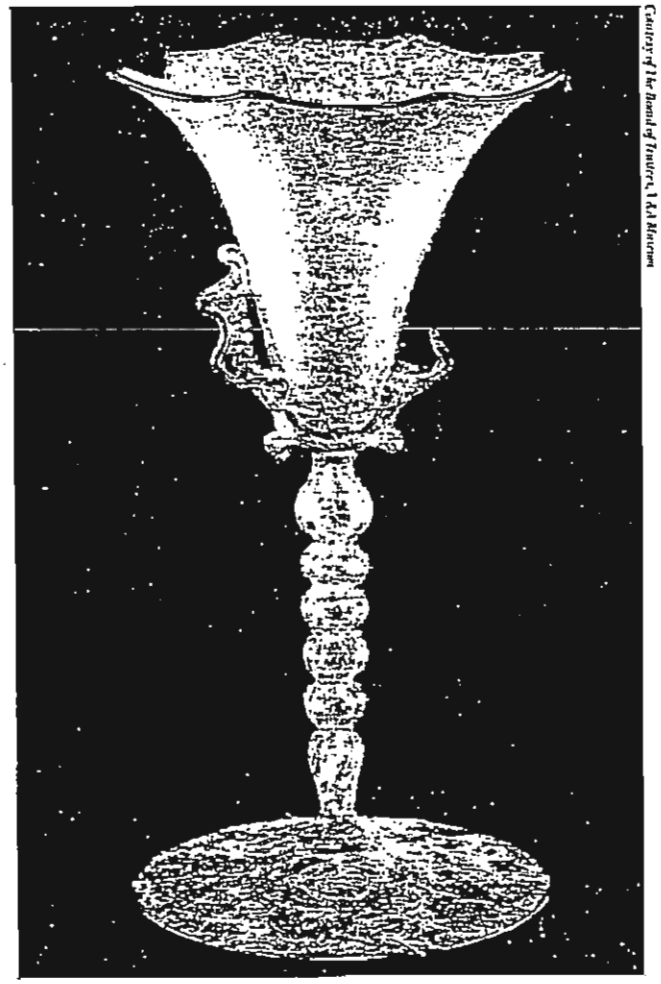
Glass Deterioration in the Museum Environment

JASON RYAN, DAVID McPHAIL, PHILIP ROGERS & VICTORIA OAKLEY

A common element in everyday life, glass is not normally associated with corrosion, but for older pieces it is a serious problem

Glass is usually thought of as a hard, brittle, transparent material that has excellent resistance to chemical and environmental attack. This is certainly true of many modern glass compositions, hence its widespread use in the building, container and telecommunications industries, although even the surface of modern glass is altered to some extent by the environment. However, it is only during the past 50 years or so that we have come to gain some clear scientific understanding of the nature of glass; a material that has been made and used by man for some 5000 years. Without the advantage of our current scientific understanding, the durability of ancient and medieval glass was rarely optimised in the rigorous way that it is today.

The main factors affecting the stability of an individual glass object are the original composition of the glass and the humidity and temperature of the environment. Like modern window and container glass, early glass consists of silica together with substantial amounts of alkali oxides, such as soda and potash, and alkaline earth oxides, such as lime and magnesia. The alkali oxides effectively break up the strongly bonded silica network thereby reducing the silica's melting point, while the alkali earth oxides stabilise the glass and increase its resistance to moisture. When a soda-lime-silica glass comes into contact with an aqueous solution, chemical and physical changes take place at the surface which can lead to the deterioration of the glass. With glass compositions that are particularly susceptible to decay, the presence of atmospheric moisture is often enough to cause the onset of deterioration.



Courtesy of the Board of Trustees, V&A Museum

Fig 1 Severely crizzled 17th century Venetian wineglass

The mechanisms by which glass deteriorates are complex. In the early stages of decay, an ion-exchange reaction occurs between hydrated protons from water molecules in the atmosphere and alkali ions from the near surface regions of the glass. As alkali ions are replaced by hydrated protons in the glass surface, an increasingly alkali-deficient, hydrated surface layer is created.

The replacement of alkali ions with smaller hydrogen ions results in the surface being placed under tensile stress. This stress is restrained by the bulk of the glass object and can lead to the initiation of micro-cracks within the near surface layer. Such cracks propagate under the influence of an applied stress as a function of relative humidity. Subsequent dehydration of the object can cause further shrinkage of the altered layer, causing cracks to open up and, in extreme cases, flakes of glass to spall away from the surface. If the alkaline corrosion products are not removed from the surface of the glass they can combine with water forming a strongly alkaline leaching solution, ultimately enabling dissolution of the silica matrix.

A large amount of work concerning the durability of glass has been undertaken worldwide, although mainly concerned with the accelerated ageing of modern glass under laboratory conditions. These tests usually involve grinding the sample into a powder in order to increase its reactivity and therefore do not always give a complete picture of the complex processes occurring at the surface and in the leached surface layers. The durability of glass is dependent on many variables including the effective surface area of the glass, the volume and pH of the leaching solution, the ions present in the corrosive solutions and their concentrations, and the humidity and temperature of the environment. The interdependency of these parameters and the fact that a number of them will change during an experiment as the glass is constantly modified by its reaction products must also be considered.[1] Much the same thing occurs during the melting of glass, as the interaction of

raw materials produces constantly changing products that consequently modify the nature of the melt.

It is evident that the problem, even with modern glass, is extremely complex, and any attempt to isolate and study any one aspect of glass corrosion in detail will require well considered and designed experimental techniques. However, considering the nature of ancient glass, with its complex composition and varied thermal and environmental history, the problem takes on an added dimension.

Glassmakers and investigators have long recognised the inherent instability of glasses. Indeed, it is reasonable to assume that the desire to overcome the problem of instability was an important driving force behind the evolution of glass as a decorative and functional material, in turn inducing a greater understanding of the nature of the material, and ultimately enabling its use as an important aid in the advancement of science.

Up until the medieval period in Western Europe and the East, soda was the dominant alkali. Soda was obtained from natural sources, such as from dried seas and lakes and from the evaporation of sea and river water, or was added in the form of a sea plant ash. In mainland medieval glassmaking centres such as in Germany and Bohemia, potash, obtained from woodland sources such as beech wood and bracken, superseded soda as the main source of alkali.[2] Whether or not lime was intentionally added to stabilise the glass is open to debate, although Susan Frank at Sheffield University has suggested that many sands used in glassmaking contained too much lime, resulting in unstable glass compositions.

In the seventeenth century, Antonio Neri wrote in his book *L'Arte Vitraria* that the finest crystal-clear glasses could only be produced from constituents that had been purified to the highest standard.[3] According to Neri, crude plant ash was finely crushed and boiled repeatedly with successive quantities of water. The extracts were then ladled into earthenware bowls to settle, and the resulting clear liquid was evaporated until crystallisation occurred. Alkali produced in this way gave a more clear and brilliant glass, but stabilising calcium and magnesium carbonates and phosphates were removed, often resulting in less durable glass compositions.[2] It is clear that Neri had some understanding of the consequences of purifying the raw materials when he states that:

> '... *in the finest glasses, wherein the salt is most purified, and in a greater proportion of salt to the sand, you shall find that such glasses standing in subterraneous and moist places will fall to pieces, the union of the salt and the sand decaying.*'

The susceptibility of much 16th and 17th century Venetian glassware to decay is largely a result of such purification processes, whereby stabilising constituents such as lime and magnesia that are less soluble than alkalis, were removed.

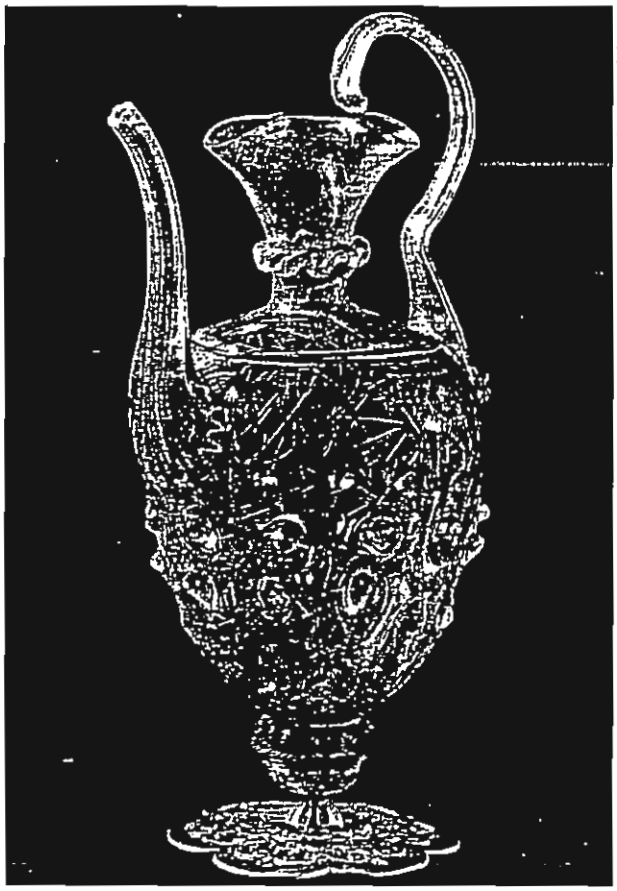


Fig 2 17th century Venetian or Netherlandish glass ewer. Note the corrosion of the gilded copper foot resulting from reaction with corrosion products from the glass

Courtesy of The Board of Trustees, V&A Museum

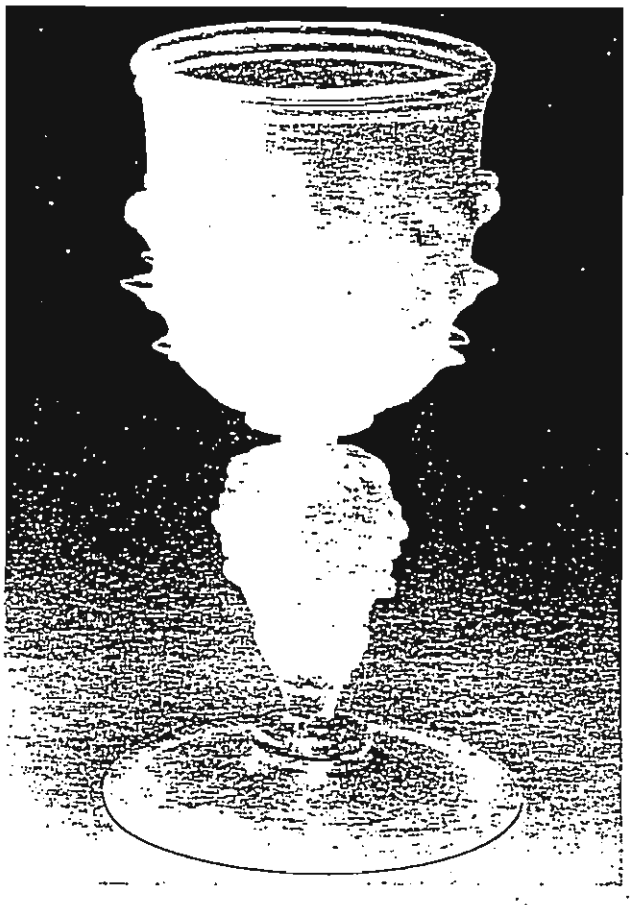
Despite an awareness of the instability of glass, the explanations of glassmakers and investigators into the phenomenon not always proved to be as accurate as Neri's observations. Bernard Pallisey, writing in 1563, tells of how the French glaziers, on observing the decay of church windows, put the phenomenon down to the effect of the sun and the moon.[4] James Fowler's *The Process of Decay in Glass* is perhaps the first serious attempt to explain and classify the symptoms of glass deterioration. He notes that 'distilled water boiled for a long time in glass vessels become(s) alkaline', and that 'this action takes place with greater ease in proportion as the glass is rich in alkalis.'[4]

In the latter [illegible] the seventeenth century, George Ravenscroft noticed that his attempts to produce glass with improved clarity and brilliance did not always result in a stable end product, when after a few months he found that some pieces had a tendency to crizzle*.[5] David Watts at Guy's Hospital Medical School suggests that Ravenscroft may have experimented with the addition of roasted tartar, from wine vats and barrels, and purified potash to remedy the problem of crizzling before he began to experiment with lead oxide, although the progressive increase of lead oxide was the major remedy to the problem.[6]

The natural process of glass decay has also long posed a serious problem to collectors and curators of glass objects. A recent survey of the condition of glass vessels belonging to the Victoria and Albert Museum in London found that about 10 per cent of the collection is showing some signs of deterioration, ranging from surface moisture through to extreme crizzling.[5] The survey also reveals that some groups of glasses are particularly vulnerable, ranging from vases and goblets from sixteenth and seventeenth century England, Spain and Italy to modern 'designer' glass from Italy and Scandinavia. The full extent of the problem has been investigated by Stanislav Ulitzka at the University of Erlangen-Nürnberg, who collected information on the state of glass collections from 17 museums worldwide. He found that all but two of the museums have a significant number of glass objects that are exhibiting some form of deterioration.[7]

Regarding museum objects, the visual symptoms of dete

*The term 'crizzle' has been applied to decayed glass since at least the 16th century. The common usage of the word was to describe the roughening of surfaces, or the crackling of sunburnt skin on the face and hands.



Courtesy of the Board of Trustees, V&A Museum

Fig 3 Late 17th century Venetian or English wineglass suffering from alkali corrosion

ration may vary considerably from one object to another. Early indicators of decay include the appearance of alkali salt deposits and the presence of moisture on the surface of the vessel. The appearance and form of the deposits may vary from a dulling or clouding of the surface to the presence of discrete salt crystals. Under humid conditions, the hygroscopic alkali deposits may deliquesce, rendering the surface slippery to the touch. In some cases, discrete droplets may form on the surface. This effect is commonly known as 'weeping'. The advanced stages of glass vessel deterioration is often referred to as crizzling. This is when the glass has developed a network of fine surface cracks. Often small pieces of glass spall away from the surface, giving the glass vessel a rough, sugary appearance.

Robert Brill of the Corning Glass Museum drew attention to a group of glasses that do not exhibit any obvious signs of decay, but which undergo a rapid surface deterioration when they are exposed to dehydrating conditions. He used the phrase 'incipient crizzling' to describe this metastable state of decay. These are glasses that have taken up water over the years to become hydrated and equilibrated with their surrounding environment. If these objects are moved to drier environments and are allowed to dehydrate, for example, if they are moved into brightly-lit, centrally heated galleries, fissures in the surface may open up, propagating a network of cracks across the surface. Glasses of this type have been known to become severely crizzled over a period of a few months.

Conservators have yet to find a satisfactory solution to the problem posed by glass decay. The deterioration, once underway, cannot be reversed and, if left unchecked, may ultimately cause the vessel to lose its mechanical strength and collapse. At present the process may only be slowed down, or at best temporarily halted, by controlling the environmental conditions of those objects that are particularly vulnerable.

Most previous research concerning the deterioration of artistic and archaeological glass has used glass samples of similar composition to the actual objects that are under investigation. However, despite the similarity in chemical composition between the glass object and the replica glass, it should be realised that the nature of the replica glass will invariably differ from that of the original. This is because of a number of factors including: (a) the use of chemically-pure powders, as opposed to the compositionally diverse raw materials used by ancient glassmakers; (b) the melting of the glass batch, usually in platinum crucibles inside laboratory furnaces, in contrast to the traditional melting process, usually carried out in refractory crucibles inside wood-burning furnaces; (c) the difference in the melting conditions as a result of the use of modern electric furnaces such as the temperature, oxidation conditions, and the time of melting; (d) the fact that most glass vessels were blown and worked by the glassmaker, whereas model glass samples are usually cast as flat plates; (e) any subsequent processing employed by the glassmaker that caused changes in the nature of the glass surface, such as annealing and fire-polishing; and (f) the fact that the glass objects have long and varied thermal and environmental histories and any investigation, no matter how complex, cannot hope to discover, let alone recreate such conditions.

The most common method of studying corrosion mechanisms in modern glass is to conduct accelerated ageing experiments. One method of accelerating deterioration is simply to

Fig 4 Close up of the foot of the late 17th century Venetian or English wineglass (Fig 3) showing the build up of alkali corrosion products

raise the temperature of the environment. This increases both the inward and outward diffusion of alkali and water molecules, and the rate of attack of aggressive agents. However, at elevated temperatures, it is likely that many reactions come into play that would not necessarily do so at room temperature.

Fig 5 Scanning electron micrograph of the surface of a crizzled Venetian goblet (x50), the pale areas are where glass has spalled away. The pale colour is the result of the build up of reaction products in the spalled areas

In order to yield worthwhile results from experimental work performed on replica glass samples, the work should be designed to simulate the conditions to which glass objects have been subjected as closely as possible. Obviously we cannot know the full thermal and environmental history of each glass vessel in the collection and, in any case, an exact simulation could take many centuries, depending on the piece. For the study of museum glass, it is perhaps more appropriate to accelerate glass deterioration under cyclic humidity conditions, as these conditions, caused by yearly, and even daily cycles of high and low relative humidity, are thought to be the main cause of crizzling in the museum environment. The importance of the cyclic nature of temperature and humidity has been indicated by a number of authors.[9, 10]

An investigation into the corrosion mechanisms involved in the decay of museum glass vessels is currently being undertaken as a joint venture between Imperial College and the Victoria and Albert Museum. On a fundamental level, the work is aimed at extending our knowledge of the decay processes of museum glass, particularly the interaction of ion-exchange processes and crack propagation. This knowledge will invariably be of use to the conservator whose aim is to halt the decay process. Only when a greater understanding of the processes has been achieved can the problem be dealt with in a systematic, safe and effective manner. On a practical level, the work undertaken will highlight susceptible glass objects and will yield information relating to their safe storage and display conditions, care and possible treatment.

Fig 6 Scanning electron micrograph of the surface of a crizzled Venetian goblet (x350), a small section of the outer layer is spalling away from the bulk glass

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THE SIGNIFICANCE OF THE REFRACTIVE INDEX OF ADHESIVES FOR GLASS REPAIR

Norman H. Tennent and Joyce H. Townsend

FILE Glass

1 INTRODUCTION

The dual aim of the restoration of glass objects is to achieve a secure and aesthetically pleasing repair. In the past, it was often necessary to sacrifice appearance to the safety of the object by using metals, for example, to secure broken fragments [1], but now many synthetic resins are available which can bond broken fragments unobtrusively and replace missing parts [2-5]. A refinement of this approach is to attempt to achieve an 'invisible' repair by tailoring the optical properties of the adhesive to match those of the glass to be repaired.

The main factor which determines the appearance of a crack or gap in glass is the refractive index (RI) of the glass relative to the RI of the material filling the gap. Breaks or cracks in glass appear less obvious when joined by an adhesive than when held together with air in the gap. This is because the RI of air is a worse match for glass than the RI of adhesives. The more closely the RI of the adhesive matches the RI of the glass in question, the more the repair looks like unbroken glass. Adhesives have been described which attempt to match the RI of the glass [6,7] but these reports are restricted to glasses of a specific RI: a major practical problem for glass conservators is the wide range of RI likely to be encountered with historic glasses. The meaning of RI and its consequences for glass repair will be discussed in the following sections; a more theoretical treatment and some numerical results for different types of glass are presented in the Appendix. The significance of the RI of varnishes for paintings has been reported by Feller [8] and De Witte [9].

Once this investigation had begun it became clear that very few measurements of the RI for historic glasses had been reported, and then invariably as incidental measurements. Information on the RI of synthetic resins, from manufacturers or in the conservation literature, was also found to be scanty. The range of RI spanned by glasses and adhesives was therefore unclear and the possibility of tailoring the RI of adhesives to match a specific glass was unknown. In addition, methods for measuring the RI of glasses and adhesives were not well documented in the conservation literature. It was therefore necessary to survey suitable methods for determining RI and then to apply these methods to the measurement of a wide range of glasses and adhesives. Only then could the feasibility of achieving 'invisible' repairs by choosing an adhesive with a matching RI to that of any historic or artistic glass be assessed. Each of these topics is developed in this paper.

2 REFRACTIVE INDEX

2.1 *Description and relevance to glass repair*

The RI determines, or can be used to describe, the behaviour of light when it passes from one material to another of different composition. The discussion which follows applies to transparent glassy materials (including synthetic polymers) and materials which are glossy when polished (e.g. jade, gemstones and ceramic glazes). Metals are a different case altogether.

When light in a medium of low RI, such as air, meets a medium of higher RI, such as glass, a small proportion is reflected (because of the difference in RI) and about 96% is transmitted. The eye perceives and the brain interprets this fairly small difference as a different situation from empty air, and one sees the glass object. On the other hand, were the glass to be immersed in a liquid of matching refractive index, the glass would not be visible at all. (Many conservators are familiar with this phenomenon, for when Paraloid B72 spheres are added to toluene they 'vanish' because the RI of toluene (1.496) is a fairly good match to that of Paraloid B72 (1.487).)

The amount of light reflected varies with the angle of viewing (see Appendix). An air-filled break in the object provides two air/glass interfaces and since the fracture surface is generally irregular in profile, multiple reflections can result. Furthermore, the difference in RI between air and glass gives rise to a phenomenon known as the 'critical angle': at angles greater than the critical angle all the light is reflected back from that point in the glass and the visual impression is of a small area of polished, mirror-like metal (see Figure 1 for an example of this). Reducing the difference between the RI of glass and adhesive reduces the amount of light reflected, resulting in a more transparent appearance.

RI is measured at a specific wavelength, usually that of the sodium D line (589nm), and quoted values are often denoted by n_D.

2.2 *Measurement*

Four techniques are available for measuring the RI of adhesives and glasses. The salient features of each method are summarized in Table 1.

Table 1 Techniques of RI measurement suitable for glass objects and adhesives

Technique	*Sample requirements*	*Accuracy*	*Comments*	*Example (Corning Glass Standard 'B')*
Rayner Refractometer, normal mode	Specimens with smooth flat surface ≥ 10mm x 4mm	± 0.003	Suitable for adhesives, stained glass and certain objects with flat areas	1.533 ± 0.003
Rayner Refractometer, distant vision	Curved specimens which allow minimal surface contact	± 0.01	Not the preferred method but suitable if other methods are not possible	1.53 ± 0.01
Abbé Refractometer	Specimens with polished flat surface ≥ 15mm x 15mm	± 0.0005	Cannot be used for most historic glasses, but the preferred method for adhesives	1.5342 ± 0.0005
Immersion	Specimens equivalent to the size of a grain of salt or less	± 0.003*	Suitable for broken glass or objects where sampling is possible. Also suitable for adhesives which do not dissolve in the immersion liquids	1.533 ± 0.003

* For immersion liquids spaced in units of 0.01

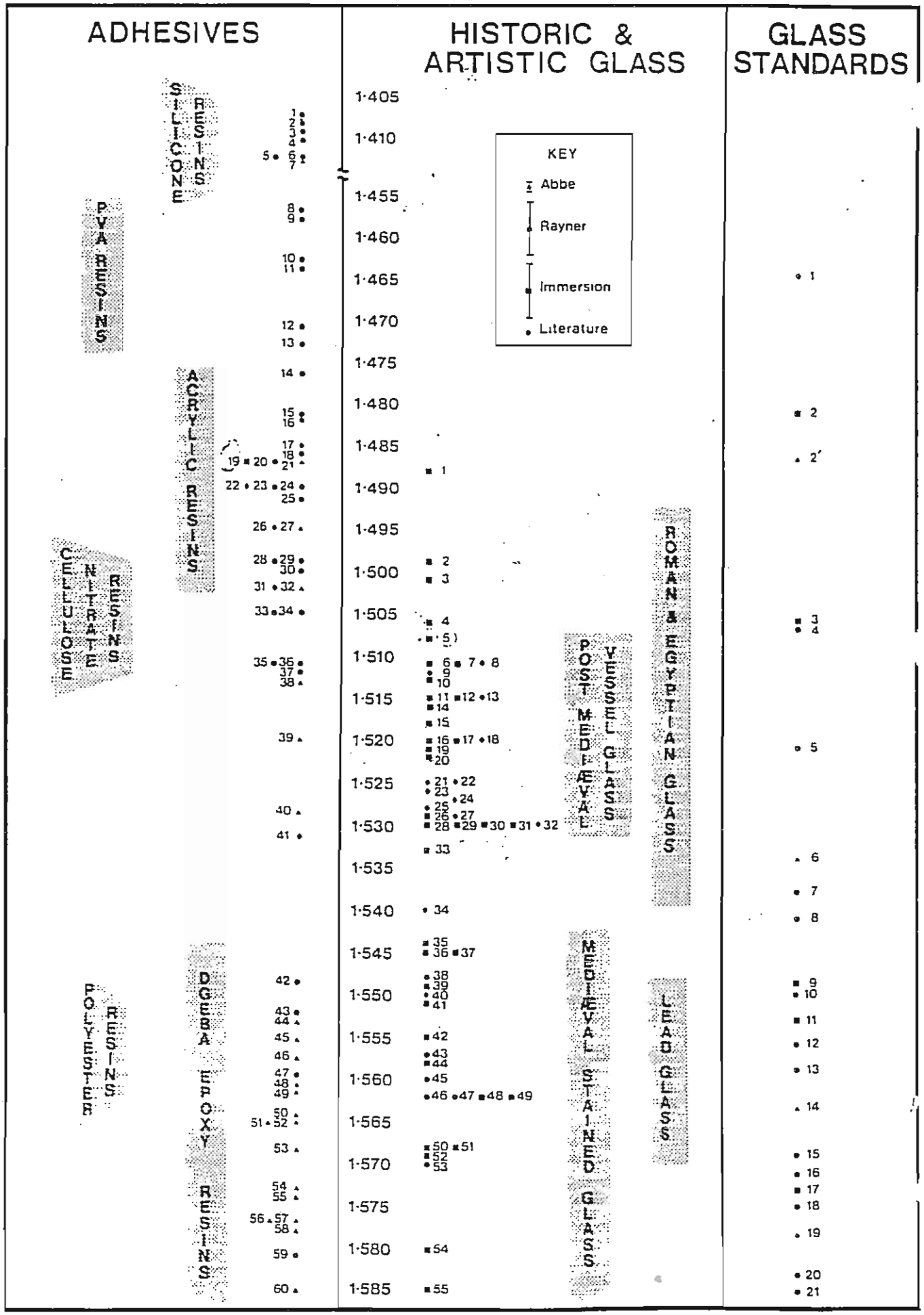
ADHESIVES
HISTORIC & ARTISTIC GLASS
GLASS STANDARDS
SILICONE RESINS
PVA RESINS
ACRYLIC RESINS
CELLULOSE NITRATE RESINS
POLYESTER RESINS
DGEBA EPOXY RESINS
POST MEDIÆVAL VESSEL GLASS
ROMAN & EGYPTIAN GLASS
MEDIÆVAL STAINED GLASS
LEAD GLASS
KEY
Abbe
Rayner
Immersion
Literature
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Table 2

Key to Table 2

ADHESIVES

1	Arbosil Aquarium Sealant (*silicone*).	Adshead Ratcliffe & Co. Ltd. Belper. Derbyshire DE5 1WJ. UK.
2	Eccosil 2 CN (*silicone*).	Emerson & Cuming (UK) Ltd. 1 South Park Road. Scunthorpe. South Humberside DN17 2BY. UK.
3	Silastic 732 RTV (*silicone*)	Dow Corning Ltd. Reading Bridge House. Reading. Berks RG1 8PW. UK.
4	Dow Corning 3140 RTV (*silicone*)	
5	Dow Corning 3144 RTV (*silicone*)	
7	Sylgard 184 (*silicone*)	
6	Loctite Clear Silicone Sealant (*silicone*)	Loctite UK. Loctite Holdings Ltd. Watchmead. Welwyn Garden City. Herts AL7 1JB. UK.
30	Loctite 357 (*UV curing, urethane acrylic*)	
33	Loctite 350 (*UV curing acrylic*)	
38	Loctite 'Glass Bond' (*UV curing system*)	
8	Rhodopas M (*PVA*): after casting	Rhodia (UK) Ltd. 14 Essex St. London WC2R 3AA. UK.
10	from solution (8). as supplied (10)	
9	Vinalac 5254 (*PVA*).	Vinyl Products Ltd. Mill Lane. Carshalton. Surrey. UK.
11	UHU 'All-purpose' (*PVA*).	Beecham UHU. Brentford. Middlesex. UK.
12	Evostik 'Resin W' (*PVA*)	Evode Ltd. Common Road. Stafford. UK.
35	Evostik 'Clear' (*cellulose nitrate*)	
13	Berol 'Merlin' (*PVA*).	Berol Ltd. Oldmedow Road. King's Lynn. Norfolk. UK.
14	Paraloid F10 (acrylic)	Rohm & Haas (UK) Ltd. Lennig House. 2 Mason's Avenue. Croydon CR9 3NB. UK.
15	Paraloid B72 (acrylic): after	
19	casting from solution (15). as supplied (19)	
16	Paraloid B82 (*acrylic*)	
18	Paraloid B67 (*acrylic*)	
20	Paraloid B66 (*acrylic*)	
23	Paraloid A30 (*acrylic*)	
25	Paraloid B44 (*acrylic*)	
17	Butvar B76. B79 (*polyvinyl butyral. PVB*)	Monsanto Ltd. Monsanto House. 10-18 Victoria Street. London SW1 0NQ. UK. (Manufacturer's data)
22	Butvar B72. B74. B90. B98 (*PVB*)	
26	Formar 12/85 (*polyvinyl formal. PVF*)	
31	Formar 5/95E. 6/95E. 15/95E (*PVF*)	
21	Plastogen G (*acrylic*)	Frank W. Joel Ltd. Oldmedow Road. Hardwick Industrial Estate. King's Lynn. Norfolk PE30 4HH. UK.
28	Durafix (*cellulose nurate*)	
34	HMG (*cellulose nitrate*)	
36	Frigilene (*cellulose nurate*)	
37	Ercalene (*cellulose nurate*)	
40	Rutapox 1200 (*epoxy*)	
44	Plastogen EP (*epoxy*)	
57	Rutapox 1210 (*epoxy*)	
24	Lascaux Acrylglasur 40X (*acrylic*).	Alois K. Diethelm Farbenfabrik. CH-8306 Brüttisellen. Switzerland.
27	Technovit 4004A (*acrylic*).	Rubert & Co. Ltd. Dennings Road. Cheadle. Cheshire. UK.
29	Bostik 5293 adhesive (*cellulose nitrate*).	Bostik Ltd. Ulverscroft Road. Leicester LE4 6BW. UK.
32	L R White Resin (*acrylic*).	London Resin Co., PO Box 24. Basingstoke. Hants RG22 5AS. UK.
39	HXTAL NYL-1 (*epoxy*)	Conservation Materials Ltd. 340 Freeport Blvd. Sparks. NV 89431. USA.
50	Ablebond 342-1 (*epoxy*)	
51	Devcon '2-ton' (*epoxy*)	
52	Devcon '5-minute' (*epoxy*)	
41	Opticon UV-57 (*UV-curing system*).	Opticon Chemical. PO Box 2445. Palos Verdes Peninsula. CA 90274. USA [6].
42	Norland Optical Adhesive 63 (*UV-curing system*)	Leader House. 117-120 Snargate Street. Dover. Kent CT17 9DB. UK.
47	Norland Optical Adhesive 61 (*UV-curing system*)	
59	Vitralit DAC (*UV-curing system*)	
43	Tiranti Embedding Resin (*polyester*).	A. Tiranti Ltd. 20 Goodge Place. London W1. UK.
45	Epotek 301 (*epoxy*).	Epoxy Technology Inc., 65 Grove Street. Watertown. MA 02172. USA.
46	Metset Resin SW (*polyester*): first batch (46). second batch	Metallurgical Services Laboratories Ltd. Reliant Works. Brockham. Betchworth. Surrey RH3 7HW. UK.
48	(48).	
49	Araldite MY790/X83-19/DY040 (*epoxy*)	Ciba-Geigy Plastics and Additives Co., Plastics Division. Duxford. Cambridge CB2 4QA. UK.
55	Araldite AY103/HY951 (*epoxy*):	
58	first batch (55), second batch (58)	
60	Araldite AY105/HY951 (*epoxy*)	
53	Epofix (*epoxy*).	Struers. Copenhagen. Denmark.
54	CXL (*epoxy*).	Resin Coatings Ltd. Colebrand House. 20 Warwick Street. Regent Street. London W1R 6BE. UK.
56	Permabond E27 (*epoxy*).	Permabond Adhesives Ltd. Woodside Road. Eastleigh. Hants SO5 4EX. UK.

HISTORIC & ARTISTIC GLASS*

1	GMAG/DA/96.38a. *Cristallo* (greenish) Venetian Tazza. 16th century.
2	NHT. Clear (2) and violet (3) glass from Alexandrine
3	*Zwischengoldglas* fragment. 1st century AD.
4	GMAG/BC/17.64. Dark blue transparent glass from Roman bottle. early centuries AD.
5	R/NM10754.248. Bohemian glass. wheel engraved. mid-18th century.
6	GMAG/DA/97.50bv. Spanish (Catalonia) jug. clear glass.
28	18th century: vessel glass (6). ornament glass (28).
7	NHT. Clear glass from Islamic lamp fragment. 13th/14th century AD.
8	Egyptian vessel stamp. 8th century AD [19. Table 1].
9	Eleven Egyptian vessel stamps. coin weights. etc., 8th century AD [19. Table 1].
10	NHT. Clear glass from Islamic lamp fragment. 13th/14th century AD.
11	R/NM10754.270. Russian (?) covered beaker. wheel engraved. mid-18th century.
12	GMAG/A/03.185gp. Cypriot glass flask. early centuries AD.
13	Egyptian beads: one pale green from Tell Asmar. 2700-2500 BC [15. p.10. specimen no.7]; two blue from Qau. 7525 [16].
14	NHT. Transparent amber (14) and blue (16) glass from
16	Alexandrine lozenge-shaped decorative glass. *c.* 1st century AD.
15	R/NM8326. Bohemian glass. wheel engraved. 1725-1750 AD.
17	GMAG/A/03.185iz. Cypriot glass dish. early centuries AD.
18	Egyptian blue bead from Tell el-Amarna. XVIII Dynasty [16].

* Explanation of registration codes: GMAG/DA. GMAG/BC. GMAG/A = Glasgow Museums and Art Galleries. Department of Decorative Art. Burrell Collection. Department of Archaeology. respectively: NHT = author's collection: R = Rijksmuseum. Amsterdam.

19 GMAG/DA/97.50cq. Southern Spanish bull-shaped ornament, green glass, 19th century?

20 GMAG/DA/97.50bu. Spanish (Catalonia) jug, clear glass, 16th century?

21 Three Egyptian red beads from Armant, 1200A [16]. XII Dynasty.

22 Egyptian vessel stamp, early-middle 8th century AD [19, Table 1].

23 Egyptian ring weight, 8th century AD? [19, Table 1].

24 Egyptian green glass bead from Qau, 612 [15, p.14, specimen no.1]. XI Dynasty [16].

25 Egyptian coin weight, early 9th century AD [19, Table 1].

26 GMAG/DA/96.38c. Venetian wine glass, late 16th century.

27 Egyptian coin weight, late 8th/early 9th century AD [19 Table 1].

29, 54 GMAG/DA/93.93w. Blue (29) and opal (54) glass from Venetian wine glass, 16th/17th century.

30 NHT. Transparent dark blue vessel glass fragment, Tell el-Amarna, XVIII Dynasty.

31 GMAG/BC/17.49. Pale green glass from Roman jar, early centuries AD.

32 Arabic bead from Assint, probably 14th-18th century AD [16].

33 NHT. Transparent turquoise vessel glass fragment, Tell el-Amarna, XVIII Dynasty.

34 Transparent pink bead from Armant, 1200A [16].

35, 36, 37, 55 Excavated mediaeval stained glass from St Andrews Cathedral (35; StA1) and Elgin Cathedral (36; EC4, 37; EC5, 55; EC1). See [17] for analytical data.

38 GMAG/BC/45.470. Clear glass from Flemish roundel, early 16th century.

39 GMAG/DA/97.50bo. Spanish (Andalusia) vase, green glass, 17th century.

40 Clear dark blue bead from Armant, 1213D [16].

41 GMAG/DA/27.90e.3. Water-glass, Scottish (John Baird Glassworks), *c.* 1881.

42 GMAG/BC/45.484. Clear, blue and green glass from German (Nuremburg) stained glass panel, *c.* 1470-1480.

43 GMAG/BC/45.462. Clear glass from Flemish roundel, 16th century.

44, 49 GMAG/DA/88.65a. Clear (44) and yellow (49) glass from ruby glass goblet, Rhine Glass Works Co., *c.* 1888.

45 GMAG/BC/45.17. Clear glass border dated 1577 (enclosing a 14th century roundel).

46 GMAG/BC/45.551. Clear glass from Dutch panel, dated 1686.

47 GMAG/BC/45.499. Clear glass from Swiss panel, late 16th century.

48 GMAG/BC/Inv 151. Wine glass, Dutch/British, mid-18th century.

50 R/NM10754.78. Wine glass, stipple engraved, Dutch, late-18th century.

51 R/NM4015. Wine glass, diamond engraved, English, 1725-1750.

52 R/RBK 1966.61. Wine glass, wheel engraved in Holland, English, *c.* 1750.

53 GMAG/45.32. Clear glass from English panel, 14th century.

GLASS STANDARDS

1 Glass FK3: Schott Glaswerke, Hattenbergstrasse 10, D-6500 Mainz, W. Germany.

2,2'	Glass Standard No 4	Society of Glass Technology, 20 Hallam Gate Road, Sheffield S10 5BT, UK.
3	Glass Standard No 5	
11	Glass Standard No 3	
4	Zinc Crown, ZC 508612	Pilkington Brothers plc, Research & Development Laboratories, Ormskirk, Lancashire L40 5UF, UK.
5	Hard Crown, HC 524592	
7	Extra Light Flint, ELF 541472	
8	Extra Light Flint, ELF 548456	
15	Light Flint, LF 567428	
19	Light Flint, LF 579411	
6	Glass Standard B	Standards prepared for the Corning Museum to simulate the composition of ancient glasses [21].
9	Glass Standard D	
10	Standard 76-C-151	Series of synthetic mediaeval stained glass compositions prepared by Pilkington Brothers for Professor R.G. Newton [22].
12	Standard 76-C-158	
13	Standard 76-C-149	
14	Standard 76-C-144	
16	Standard 76-C-150	
17	Standard 77-C-33	
18	Standard 76-C-145	
20	Standard 76-C-147	
21	Standard 76-C-148	

A description of the Abbé refractometer and its mode of operation is available in standard optics textbooks [10]. The authors have found the Rayner refractometer to be an attractive, cheaper, simpler and more versatile alternative, though not capable of the accuracy of the Abbé. RI measurements made to ±0.003 are, however, of more than adequate accuracy for the selection of matching adhesives for glass repair. The immersion technique is widely used for mineralogical studies and is also well described in many textbooks [11,Ch.3; 12,Ch.3]. It is based on the observation of a tiny sample through the microscope (40-50x magnification): a series of liquids of known RI is used to immerse the sample until a liquid is found in which the sample disappears. The selection of the relevant immersion liquid is facilitated by observing the behaviour of the Becke line [11,12]. Immersion liquids are available commercially in steps of 0.005 or 0.01. Alternatively, a graded series of liquids of varying RI can be prepared by mixing two terminal liquids [13,14]. The properties which these liquids should possess are well documented [14]; mixtures of butyldigol (RI 1.431-1.433) and 1-chloronaphthalene (RI 1.632-1.634) are suitable for the work described in this paper.

Adhesives were examined primarily with the Abbé refractometer or, for less accuracy but greater convenience (since sample quality is of less importance), the Rayner refractometer. A sodium lamp, or a suitably filtered light source, was used. The adhesives were either cast and polished or prepared as a thin film either on a glass microscope slide or directly on the prism of the refractometer. In the former instances the contact liquid, 1-chloronaphthalene, may dissolve some resins. In certain cases the resin was examined by immersion, but this method was found to be more useful for glasses where a tiny fragment can be removed from a broken piece. Even for intact glass objects, sufficient sample can usually be removed unobtrusively by means of a diamond-tipped probe.

3 RESULTS

3.1 *The refractive indices of adhesives and glasses*

The results of RI measurements on a variety of adhesives, historic glasses and glass standards are presented in Table 2. Specific results are plotted individually and may be identified by means of the key to the Table. Examination of these measurements shows up certain groupings of adhesives and glasses, and these are indicated in the Table by the shaded areas, the terminal points of which are somewhat uncertain.

It is clear from the Table that historic and artistic glasses span a wide range of RI, principally from *c.* 1.480-1.580, which indicates the problems of tailoring the RI of an adhesive to match closely that of a glass requiring restoration. Fortuitously the span of glass RIs is well matched by that of different classes of synthetic polymers; for example, most amine-cured epoxy resins examined fall in the useful RI range 1.550-1.585, but silicone resins span the range 1.405-1.415, and are therefore unsuitable for giving a close RI match for glass repair. (It is an interesting and useful offshoot of this work that polymer classes and glass types can often be identified on the basis of their RI. This is not surprising, since the RI is a consequence of composition, though in the case of glasses, density is a more suitable probe for characterization purposes. Weathering and the annealing process can both affect the RI of glasses [18,19].)

The grouping of historic glasses includes some literature values. Although few measurements of RI for historic glasses have been published, data are available on several dozen glass artifacts and experimentally-melted counterparts of similar compositions, which will be published in due course [20]. The values for historic glasses in Table 2 are mirrored by those for specially prepared glass standards, designed to simulate the compositions of early glasses [21,22].

The RIs of several adhesives and glasses were determined by more than one method. Agreement was within experimental error (see, for example, Table 1).

It has been found that the RI of adhesives changes during cure or drying, so during the restoration of glass the initial appearance of the repair will be modified. The values given in Table 2 are for fully cured resins or solvent-borne resins after several days' drying. Adhesives from the latter group may never regain the RI of the resin prior to the addition of solvent. The RI of Rhodopas M PVA resin, for example, was 1.451 ± 0.003 immediately after preparation, 1.455 after several days and 1.457 after several years. The RI of the resin as supplied was 1.463. This illustrates the plasticizing effect of the solvent, which was still noticeable in the oldest sample.

Although the proportions of hardener and resin can affect the RI (see section 3.3), good consistency (variations of ± 0.001) was shown by several Ablebond 342-1 epoxy resin samples prepared with the same proportion of resin to hardener. Different batches of Metset SW polyester resin showed equally high consistency in RI.

The dispersion (a slight variation of RI with wavelength throughout the visible spectrum) of glasses and adhesives has not been studied. It can be assumed that this, and the very small temperature dependence of the RI, will be swamped by other causes, namely batch-to-batch variation in adhesives and variations due to working the glass surface during the manufacture of the object.

3.2 *The effect of matching the refractive index of adhesives and glass*

Figure 1 illustrates the significance of RI in the repair of a cracked lead glass vessel (RI 1.558 ± 0.003) by means of clear, low viscosity resins. For this repair, two different water-white epoxy resins were used to fill the crack which runs from the rim of the vessel to its base.

Ablebond 342-1 was selected from Table 2 as an adhesive whose refractive index, 1.5646 ± 0.0005, matches very closely the glass in question. The resin was applied carefully along the upper half of the crack and was drawn in by capillary action. As the resin penetrated, the crack immediately became less visible. The excess resin was wiped away from the surface of the glass and the vessel set aside for two days at room temperature to allow the resin to cure fully. By this time only a very faint hairline could be seen to indicate the position of the break. (A chip half way along this section of the crack was not filled and remained quite visible (Fig. 1b).)

HXTAL NYL-1, an epoxy resin of equal water-white clarity to Ablebond 342-1 but whose RI, 1.5201 ± 0.0010, differed from the glass by 0.038, was used to fill the remainder of the crack down to the base of the vessel. The same procedure was adopted, but since this resin cures very

a

b

Fig. 1 Modern lead glass bowl (RI 1.558) before (a) and after (b) repair with Ablebond 342-1 epoxy (RI 1.565) above the arrow and HXTAL NYL-1 epoxy (RI 1.520) below it.

slowly at room temperature, seven days elapsed before cure was complete. For this resin the crack also appeared less visible than before restoration, especially at certain angles of viewing. At other angles, however, total internal reflection of light occurred (see section 2.1) and the crack appeared as a silvery line (Fig. 1b). This was not the case with the part of the crack mended with Ablebond 342-1.

It is clear, therefore, that for resins chosen to match as closely as possible the RI of broken or cracked glass, the quality of the repair is superior to cases where a mismatch of even 0.04 occurs.

3.3 *Modification of the refractive index of commercial adhesives*

While the range of commercial adhesives given in Table 2 is a good starting point for the selection of an adhesive which matches the RI of any given glass object, there remain instances where this tabulation might not permit a suitable adhesive to be chosen. The Table can be extended in two ways: by the addition of new commercial products or by the ability of conservators to modify marginally the RI of a particular commercial product.

Since epoxy resins represent the most useful class of adhesive for glass bonding the investigation has been restricted to these resins. Three approaches have been explored: the effect of using different hardeners for a single epoxy resin component, the effect of marginally changing the proportion of hardener and the effect of the addition of other components, principally plasticizers and diluents. (The addition of dyestuffs does not affect the RI of a resin.) These results are reported in full elsewhere [23] but it is relevant to summarize the conclusions here.

It is possible to cure successfully a series of commercial resins based on the diglycidyl ether of bisphenol A (DGEBA) with amine hardeners other than those specified by the manufacturer. This is to be expected, since the DGEBA resin components of these epoxies are generally similar. RI variations in the range 0.011 to 0.026 were found when a set of epoxy resins was cured with alternative hardeners [23].

A factor which may play some part in these RI modifications is the ratio of hardener to resin. This factor was investigated separately and it was found that RI changes of the order of 0.003 can be produced by a variation in hardener proportion of 25% from the recommended value [23].

The addition of dibutyl phthalate was also found to affect the RI of the cured epoxy resin [23]. In fact, the presence of dibutyl phthalate is the main reason for the difference in the RI of Araldite AY103/HY951 and AY105/HY951 (Table 2).

Tampering with resin formulations in these ways creates the risk that the properties of the cured resin will be adversely affected. It has been observed, for example, that light-induced yellowing of certain resins is more pronounced when alternative hardeners are used but in other cases an improvement in light stability actually results [23]. The effect on adhesive strength has not been examined.

For crack mending, however, the tendency of a resin to yellow is of less importance than the ability of the RI to match the glass undergoing repair. A simple experiment served to prove this point: a crack in a lead glass vessel (RI 1.558) filled with a solvent of matching RI (nitrobenzene, 1.553) dyed an intense yellow colour was less visible than the same crack filled with a water-white liquid of differing RI (toluene, 1.496). It is implicit in this argument that the yellowing process does not greatly affect the RI of the resin. This has been found to be the case [23]. For restored breaks where the resin has a significant thickness, on the other hand, the yellowing of the resin can become obtrusive.

3.4 *Synthesis of adhesives with a specified refractive index*

An alternative approach, not pursued in the course of this work, is the synthesis of adhesives with predetermined RIs. This is in principle quite possible but is unlikely to become a practicable reality for most conservators. De Witte adopted this course of action [9] in order to prepare acrylic picture varnishes with a high RI. It is also relevant that copolymerization of isobutyl methacrylate and styrene in

prescribed proportions has been reported to give a graded set of mounting media for microscopical sections in the range 1.477 to 1.590 [24].

4 PRACTICAL FACTORS IN ACHIEVING A HIGH QUALITY REPAIR

In this study most visual assessments of the significance of RI in glass repair were made on cracked glass because this avoided the need to align broken fragments, but for both cracked and broken glass certain steps can be taken to ensure an optimum appearance.

4.1 *Cracked glass*

1 The adhesive strength required for bonding cracks is less than that for bonding broken fragments, so the range of suitable polymers can be extended to include classes such as acrylics which are not good adhesives for glass. It is also possible to use adhesives whose resistance to yellowing is not of the first order for very narrow cracks (see section 3.3).

2 Since there is evidence that the RI of an old crack may differ by as much as 0.235 from that of the bulk glass [25] it is advisable to refine the RI measurement, made initially by one of the methods described in section 2.2, by determining which of a series of immersion liquids drawn in by capillary action makes the crack least visible.

3 Once an adhesive of appropriate RI has been selected, a greater speed of penetration of the crack by capillary action can be achieved by warming the resin to reduce its viscosity. (For a discussion of the relevant factors involved in enhancing penetration during consolidation see [26.Ch.7].) The danger of the crack spreading if the glass itself is heated should be borne in mind.

4.2 *Broken glass*

1 Alignment of the broken fragments is all-important. Sometimes taped pieces move slightly during cure or drying of an adhesive. A valuable technique is the application of an initial small, securing spot of cyanoacrylate adhesive prior to bonding by the chosen adhesive [27]. Cyanoacrylate adhesives are not recommended as the sole adhesive for glass bonding as in time the bond will fail.

2 When bonding fragments of flat glass such as stained glass (or even gently curved pieces) it is helpful to ensure that the best fit is achieved, with the fragments lying in the correct plane, by observing the reflection of a fluorescent lighting tube in the glass. If this appears smooth and unbroken then the glass is positioned correctly.

4.3 *Cracked or broken glass*

The hairline crack which remains on the glass surface after bonding is caused by the resin creating an imperfectly smooth surface with the glass. This can be minimized by smoothing out a tiny excess of resin along the edge of the crack or break with a 12u-thick Melinex (polyethylene terephthalate) film. This can be peeled away when the resin has set. (One disadvantage of HXTAL NYL-1 epoxy resin is that it bonds so firmly to Melinex that this technique cannot be used.)

5 CONCLUSIONS

Several issues have been clarified as a result of this investigation. The range of RI spanned by adhesives and the RI values typical of historic and artistic glasses have been identified. In the course of these measurements the most suitable methods for the determination of such RIs have been ascertained. These results have been used to show that it is possible to achieve a good match between the RI of adhesives and most glasses. Experiments in the repair of glass have demonstrated that tailoring of the RI of an adhesive to that of a broken or cracked glass does enhance the quality of the repair. When a very close (± 0.003) match is achieved, invisible repairs almost become a possibility, though the ethical justification for this degree of perfection remains open to question. For most practical purposes it has been shown that a match of *c.* 0.01 can lead to an almost invisible repair, and that a mismatch of *c.* 0.04 can leave the break or crack readily visible. These findings are of most relevance to those glasses, especially post-mediaeval vessel glass, where the glass surface is not badly weathered.

It is a valuable additional conclusion of this study that RI determination provides a good means of differentiating certain polymer classes and glass types.

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SUPPLIERS OF EQUIPMENT AND MATERIALS

Rayner Dialdex Refractometer; sets of immersion liquids: Gemmological Instruments Ltd, St Dunstan's House, Carey Lane, London EC2V 8AB, UK.
Butyldigol; 1-chloronaphthalene: MacFarlane Robson Ltd, Burnfield Avenue, Glasgow G46 7TP, UK.
Melinex: Frank W. Joel Ltd, Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk PE30 4HH, UK.

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APPENDIX

The refractive index (n_2) of a medium is given by the ratio of the velocity of light in vacuum to the velocity of light in the medium. For numerical purposes, n (air) = 1, as for a vacuum. The velocity of light in any medium is less than in vacuum, so in consequence light which enters a medium of higher RI at an angle of incidence θ_1 is refracted at a smaller angle θ_2, as shown in Figure 2. For a medium of lower RI (n_1),

$$n_2/n_1 = \sin\theta_1/\sin\theta_2.$$

When light is travelling from glass to air and θ_1 reaches 90°, θ_2 is called the critical angle θ_c, and all light leaving the glass surface at θ_c or a higher angle is reflected back. This is known as total internal reflection. The critical angle is given by

$$\sin\theta_c = n_1/n_2.$$

Classical electromagnetic theory (Maxwell's equations) applied to a flat, non-magnetic air-medium boundary such as glass, leads to the result that light at normal incidence is partially reflected. The proportion reflected is given by

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)}$$

A refinement of the theory to angles of incidence other than the normal introduces polarized light (Fresnel reflection). Since the eye cannot detect polarization, the results for the two polarized components have to be summed to indicate what one would see at each viewing angle. Graphs of calculated values [28,p.400] indicate that the simpler equation given above is valid for viewing angles of 40° for soda glass in air. Some values for typical glasses are given below, in Table 3. A justification for these results is available in standard physics texts (e.g. [29]).

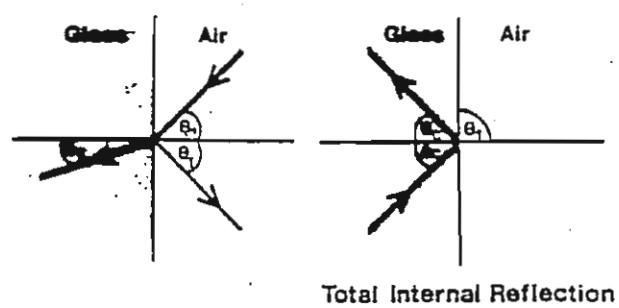

Fig. 2 Behaviour of light at an air-glass boundary.

Table 3 Calculated values of the critical angle and the percentage of light reflected, for various glasses in different media

Glass in medium of lower RI	n_2	n_1	θ_c	*R*	*Viewing angle for which R is valid*
Early glass in air	1.45	1.00	44°	3.4%	40°*
Soda glass in air	1.52	1.00	41°	4.3%	36°*
Soda glass in matching adhesive	1.52	1.51	83°	0.00001%	+
Lead glass in air	1.58	1.00	39°	5.1%	33°*
Lead glass in matching adhesive	1.58	1.57	84°	0.00001%	+

* From [28,p.401].
\+ R = 0.1% at 80°, 6% at 85°, and much less at lower angles.

RELEVANT ADHESIVE TERMINOLOGY

Adherend
A body that is, or is intended to be, held to another body by an adhesive.

Anaerobic adhesive
A polymerizable adhesive that is intended to polymerize spontaneously in the absence of oxygen, the polymerization being substantially inhibited by the presence of oxygen.

Animal glue
See 'glue'.

Binder
The component of an adhesive composition that is primarily responsible for the forces that hold the adherends together.

Body (noun)
A subjective assessment of consistency (q.v.)

Body (verb)
To thicken an adhesive.

Bond (noun)
An attachment between adherends achieved by an adhesive.

Bond (verb)
To attach adherends by an adhesive. *Note.* The use of 'glue' is deprecated.

Bond-line
The adhesive layer in a bonded joint. *Note.* The use of 'glue-line' is deprecated.

Bond strength
The force necessary to bring an adhesive joint to the point of failure, with failure occurring in or near the plane of the bond-line.

Breaking force
The force necessary to bring an adhesive joint to the point of failure, irrespective of mode of failure.

Brushing adhesive
An adhesive that is designed for application by brush.

Cellular adhesive
An adhesive that has been extended by the incorporation of gaseous cells; also called 'foamed adhesive'.

Cement
Inorganic adhesive materials setting by hydration, e.g. Portland cement. *Note.* The term is also used as a synonym for organic adhesive but this usage is strongly deprecated.

Close-contact adhesive
An adhesive suitable for use only in joints where the surfaces to be joined can be brought into close contact and where bond-lines do not exceed 0.1mm. *Note.* Close-contact adhesive is in contrast to gap-filling adhesive (q.v.).

Coalescence
(a) The fusion of dispersed particles of an emulsion. (b) The fusion of two adhesive films when brought together (*see* 'two-way-stick adhesive').

Cohesion
The state in which the particles of a single substance are held together by the primary or secondary valence forces.

Cohesive failure
Failure within the body of the adhesive, i.e. not at the interface.

Cold-curing adhesive
An adhesive (usually a two-part system) that cures without the application of heat.

Cold flow
Deformation of a material at room temperature without applied load (*see also* 'creep').

Cold glue
See 'cold-setting adhesive'.

Cold-setting adhesive
An adhesive that can be applied and will set at a temperature of 23°C or lower; also called 'cold glue', but this usage is deprecated.

Compressive shear
See 'shear'.

Consistency
A general term for the property of a material by which it resists permanent change of shape. *Note.* Consistency is not a fundamental property but is comprised of viscosity, plasticity and other rheological properties.

Contact adhesive
An adhesive that is applied to both adherends and allowed to become tack dry (q.v.) before the joint is closed. It develops strength immediately the joint is closed, no sustained pressure or setting time being required. *Note.* These materials are known in the stationery industry as 'self-seal adhesive'.

Creep
The slow inelastic deformation of an adhesive layer under load, following the initial instantaneous elastic or rapid deformation (*see also* 'cold flow').

Cure (verb)
To increase the cohesive strength of an adhesive through chemical changes, e.g. polymerization or crosslinking, thus developing the mechanical and physical properties for any given application.

Cure temperature
The specified temperature for curing an adhesive (*see also* 'setting temperature').

Cure time
The period of time necessary for an adhesive to cure under the specified conditions.

Double-spread adhesive
See 'two-way-stick adhesive'.

Dry tack
The property exhibited by adhesive systems when the apparently dry adhesive films will adhere themselves immediately on contact; also called 'aggressive tack'.

Elasticity
The property of the material by which it tends to return to its original dimensions after the removal of a stress.

Emulsion adhesive
A stable dispersion of a polymeric adhesive in a liquid continuous phase.

Fatigue life
The number of stress cycles necessary to bring an adhesive bond to the point of failure when the bond is subjected to repeated cyclic stressing under specified conditions. *Note.* Fatigue life depends on (a) the frequency and waveform of the applied stress; (b) the magnitude of the applied stress; (c) whether or not both compressive and tensile stresses occur within each cycle.

Fatigue strength
The force that a joint will withstand when the force is applied repeatedly for an infinite number of times. *Note.* For practical purposes, 10^7 cycles is considered to be an adequate indication.

Foamed adhesive
See 'cellular adhesive'.

Foaming adhesive
An adhesive designed to foam *in situ* after application to provide extensive gap-filling properties.

Gap-filling adhesive
(a) For high strength, load-bearing purposes, an adhesive that will provide satisfactory bond-strength in bond-lines up to 1.3mm in thickness (*see also* 'close-contact adhesive'). (b) For the construction industry, a high solids adhesive designed for use on uneven surfaces and to bond satisfactorily where there are gaps of up to 6mm.

Gel
A colloidal system of semi-solid nature, consisting of a solid dispersed in a liquid. If lyophilic (dilutable) it may be converted to a sol or liquid form, by the addition of more of the liquid phase.

Gel point
See 'gel temperature'.

Gel temperature
The temperature at which the system no longer flows under shearing stress, but shows a tendency to tear; also called 'gel point'.

Gelation
The process of forming a gel. *Note.* Adhesives can be classified by mode of gelation. (a) Gel formation by loss of volatile constituents by evaporation or diffusion: (i) loss of organic solvent, e.g. rubber solution; (ii) loss of water, e.g. starch, animal glue, rubber latex, sodium silicate, polyvinyl acetate, etc. (b) Gel formation by cooling, e.g. animal glue. (c) Gel formation by condensation polymerization, e.g. urea formaldehyde, phenol formaldehyde. (d) Gel formation by addition polymerization, induced by heat, catalyst and/or light, e.g. various polyesters.

Gelation time
The time measured from the moment the adhesive is ready for use to when the adhesive has sufficient consistency to resist flow under the conditions of the test.

Glue (noun)
e.g. animal glue, fish glue. An impure protein obtained by hydrolysis of collagenous materials such as skin, bone and connective tissue by various methods; also an adhesive prepared from this substance by heating with water. *Note.* Through general use, the term 'glue' is often synonymous with 'adhesive' but this is strongly deprecated.

Glue (verb)
See 'bond'.

Glue-line
See 'bond-line'.

Green strength
The strength of a bond determined immediately after assembly.

Gum
A water-soluble vegetable resin or its solutions in water or alcohol or a solution of dextrine in water.

Gun-applied adhesive
An adhesive that is designed for application by extrusion gun; also called 'gunnable adhesive'.

Heat-activated adhesive
A dry coating of adhesive that is rendered tacky by application of heat.

Heat activation/reactivation
The provision or restoration of the bonding properties of a dried adhesive film.

Heat seal
A joint made by reactivating a thermoplastic adhesive already present in a thin layer on the adherends (*see* 'heat-sealing adhesive').

Heat-sealing adhesive
A thermoplastic adhesive already present in a thin layer on the adherends which, by the application of heat and pressure, forms the bond.

Heat-sealing adhesive film
A heat-activated adhesive in film form. *Note.* The film may be a coating on an adherend. The term is commonly used in the packaging industry.

Hot-curing adhesive
An adhesive that cures at a temperature of 50°C or above.

Hot-melt adhesive
A thermoplastic adhesive that is applied in the molten state and forms a bond on cooling to a solid state.

Hot-setting adhesive
An adhesive that sets at a temperature of 50°C or above.

Impact strength
The force necessary (usually measured in units of energy) to bring an adhesive joint to the point of failure by means of a very high rate of stress development.

Jelly glue
A prepared adhesive consisting of a gelled solution of animal glue in water, with or without additives such as plasticizers, fillers, etc. It is melted for use.

Lap shear strength
The force necessary to bring an adhesive joint to the point of failure by means of stress applied in the longitudinal mode, parallel to the plane of the bond-line; also called 'longitudinal shear strength'.

Latex adhesive
A stable dispersion of elastomeric polymer in a water continuous phase.

Longitudinal shear strength
See 'lap shear strength'.

Mastic
A term used mainly in the construction industry for a general purpose sealant.

Mastic adhesive
A viscous gap-filling adhesive with slump-resisting properties that can be applied either by spatula or from a gun (*see also* 'mastic').

Mechanical adhesion
Adhesion between surfaces due to the interlocking of a solid adhesive with the asperities of the surfaces or subsequent solidification of a liquid adhesive absorbed by porous substrates.

Mineral glue
See 'silicate adhesive'.

Mucilage
A solution of gum in water.

Multi-part adhesive
An adhesive that is packed as two or more separate reactive components that are either mixed before use or applied separately to the adherends.

Multiple-layer adhesive
A film adhesive, usually supported with a different adhesive composition on each side, designed to bond dissimilar materials.

Negative thixotropy
An increase of the apparent viscosity under shear stress followed by a gradual recovery when the stress is removed. The effect is time-dependent. Also called antithixotropy, rheopexy.

One-part adhesive
An adhesive, sometimes prepared from several ingredients, that is packed in a single container and ready for use but which may require the addition of water.

One-way-stick adhesive
An adhesive that is applied to only one of the adherends; also called 'single-spread adhesive'.

Paste adhesive
An adhesive in paste form.

Peel
A mode of application of a force to a joint in which one or both of the adherends are flexible and in which the stress is concentrated at a boundary line.

Peel adhesion
See 'peel strength'.

Peel strength
The force necessary to bring an adhesive joint to failure and/or maintain a specified rate of failure by means of a stress applied in the peeling mode.

Polymerization adhesive
An adhesive that sets by polymerization in the assembly.

Pot life
(a) Hot-melt adhesives: the time for which an adhesive, ready for use, remains usable when kept at the normal operating temperature. (b) Multi-part adhesives: the period during which the adhesive can be used after mixing the components. This varies with volume and temperature of the mixed adhesives and the ambient temperature.

Pressure-sensitive adhesive
An adhesive that produces a permanently tacky film to which a second adherend readily adheres after the brief application of pressure; also called 'self-adhesive' but this term is deprecated.

Priming
Application of a coating to an adherend surface, prior to the application of an adhesive, to improve adhesion and/or durability of the bond.

Release agent
A coating material intended to prevent or reduce adhesion, e.g. waxy materials, silicones.

Resin
(a) A solid, semi-solid or liquid, usually organic, material that has an indefinite and often high molecular mass and, when solid, usually has a softening or melting range and gives a conchoidal fracture. *Note.* Bitumens, pitches, gums and waxes are excluded by convention. (b) A polymeric material, commonly uncompounded, used in the plastics industry.

Sealing
The application of a material to the surface of an adherend, prior to that of the adhesive, in order to reduce the absorbency of the adherend; also called 'sizing'.

Self-adhesive
See 'pressure-sensitive adhesive'.

Self-curing adhesive
A one-part adhesive that cures, after application, under specified conditions.

Self-seal adhesive
See 'contact adhesive'.

Separate application adhesive
An adhesive consisting of two parts, one part being applied to one adherend and the other part to the second adherend. The parts react when the two are brought together to form a joint.

Setting
The process by which an adhesive increases its cohesive strength by chemical or physical action, e.g. polymerization, oxidation, gelation, hydration cooling, or evaporation of volatile constituents.

Setting temperature
The specified temperature for setting an adhesive (*see also* 'cure temperature').

Setting time
The time interval between the commencement of a setting process, e.g. the application of heat and/or pressure to an assembled joint, and the development of the desired level of bond strength.

Shear
A mode of application of a force to a joint that acts in the plane of the bond-line. The force may be applied in longitudinal compression or tension or torsion.

Shear strength
The force necessary to bring an adhesive joint to the point of failure by means of forces applied in a shear mode.

Shelf life
The time of storage under stated conditions during which an adhesive may be expected to retain its working properties.

Silicate adhesive
A solution of silicate in water, usually sodium silicate; also called 'mineral glue'.

Single-spread adhesive
See 'one-way-stick adhesive'.

Size
Material used for sizing.

Sizing
See 'sealing'.

Solution adhesive
See 'solvent-borne adhesive'.

Solvent-activated adhesive
A dry adhesive, pre-applied to an adherend, that is rendered tacky just prior to use by application of a solvent.

Solvent activation/reactivation
The use of solvent to provide or restore the binding properties of a dried adhesive film.

Solvent adhesive
A solvent or dilute solution of a polymer that dissolves the surfaces of the adherends, and which bonds as the solvent evaporates (*see also* 'solvent-borne adhesive').

Solvent-based adhesive
See 'solvent-borne adhesive'.

Solvent-borne adhesive
An adhesive in which the binder is dissolved in an organic solvent (*see also* 'solvent adhesive'). Also called solution adhesive, solvent-based adhesive.

Spraying adhesive
An adhesive that is designed for application by spraying.

Stabilizer
An additive to an adhesive intended to prevent or slow down undesirable effects such as excessive reactivity, absorption by adherends, coagulation.

Structural adhesive
An adhesive used for bonding engineering structures. It is usually a high-strength adhesive based on a thermosetting polymer, capable of sustaining a combination of stresses for long periods. *Note.* The combination of stresses may, for example, include peel and shear forces, fluctuating loads, environmental exposure and steady load.

Substrate
A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than 'adherend' (q.v.).

Supported adhesive film
An adhesive supplied in a sheet or in a film form with an

incorporated carrier that remains in the bond when the adhesive is applied and used. *Note.* The carrier may be woven or non-woven material consisting of organic or inorganic fibres.

Syneresis
The exudation of small amounts of liquid by gels on standing.

Synthetic resin
An adhesive based on a synthetic monomer or polymer.

Tack (noun)
The property of a material that enables it to form a bond immediately on contact with another surface which may be an adherend or another layer of adhesive (*see* 'dry tack'). *Note.* Tack describes the ability of the adhesive surface to deform and flow, wetting the second surface immediately on contact, thereby forming a bond.

Tack dry
Exhibiting dry tack (q.v.); also called 'tacky dry'.

Tack force
The force necessary to separate the film of adhesive from a second surface. This force may increase with time as the film continues to flow. *Note.* The term 'quick stick' is sometimes used to describe the tack force immediately after the bond is made.

Tackifier
An additive intended to enhance the tack of an adhesive film, or to extend the tack range of an adhesive.

Tack range
The period of time for which an adhesive will be in the tack dry condition after application to a specified adherend under specified conditions of temperature and humidity; also called 'tack time'.

Tack time
See 'tack range'.

Tensile strength
The force necessary to bring an adhesive joint to the point of failure by means of an essentially uniform stress at right angles to the bond-line.

Tension
The mode of application of a tensile force normal to the plane of a joint between rigid adherends and uniformly distributed over the whole area of the bond-line.

Thermoplastic (adjective)
Having the property of being softened by heat and hardened by cooling; these phenomena are repeatable. Many thermoplastic materials become thermosetting by appropriate treatment to induce crosslinking, e.g. by addition of a suitable chemical crosslinking agent or by irradiation.

Thermosetting
Having the property of undergoing a chemical reaction by the action of heat, catalysts, ultraviolet light, etc., leading to a relatively infusible state. *Note.* Thermosetting resins, when cured, are generally insoluble.

Thixotropy
A decrease of the apparent viscosity under shear stress, followed by a gradual recovery when the stress is removed. The effect is time-dependent.

Two-part adhesive
A multi-part adhesive comprising two components, that are either mixed before use or applied separately to the adherends.

Two-way-stick adhesive
An adhesive that is applied to both adherends; also called 'double-spread adhesive'.

Unsupported adhesive film
An adhesive supplied in sheet, film or web, without an incorporated carrier.

Warm-curing adhesive
An adhesive that cures at temperatures between 23°C and 50°C.

Warm-setting adhesive
An adhesive that sets at temperatures between 23°C and 50°C.

Water-borne adhesive
An adhesive in which the solvent, or the continuous phase in the case of an emulsion or latex, is water; also called 'aqueous adhesive'.

Waterproof glue
See 'water-resistant adhesive'.

Water-resistant adhesive
An adhesive which, after setting in the joint, will withstand prolonged contact with water. *Note.* The term 'waterproof glue' is deprecated because it implies that an impregnable barrier to water is formed by the glue, which is very misleading.

Wet strength
The strength of an adhesive bond determined immediately after removal from a liquid in which it has been immersed under specific conditions. *Note.* The term 'wet strength' is commonly used alone to designate strength after immersion in water. In the case of some water-borne and latex adhesives the term is also used to describe the bond strength when the adherends are brought together with the adhesive still in the wet state (*see* 'green strength').

Yield stress
The stress applied to a joint at which permanent deformation occurs; also called 'yield value'.

Yield value
See 'yield strength'.

APPENDIX: SPECIFIC MATERIALS

Animal origin

Casein
Protein precipitated from skimmed milk by the action of rennet or acid. When compounded with other reactants it is used as an adhesive for wood and packaging applications.

Collagen
The natural protein of skin, bone and connective tissue from which gelatine and animal glue are obtained.

Gelatine
The soluble protein derived from collagen.

Vegetable origin

Carnauba wax
A naturally occurring wax from the leaves of the Brasilian wax palm (*Copernica cerifera*) which is frequently used as a constituent of release agents (q.v.).

Cashew-nut liquid
The liquid (steam distillate) obtained from the nut of the cashew tree, *Anacordia occidentale*, which is mainly composed of natural phenols. *Note.* The uses of cashew-nut liquid are as follows: (a) an intermediate polymer, cashew-nut phenolic resin, can be formed which reacts with paraformaldehyde to give slightly flexible products; (b) as an adhesive, in particular for abrasive grits and sand; (c) as a tackifier (q.v.).

Cellulose esters
Products of the esterification of certain of the hydroxyl groups of the cellulose macromolecule with organic or mineral acids; cellulose esters are soluble in organic solvents such as esters or ketones, and thus form the basis

of some solvent-borne adhesives. *Note.* Examples of cellulose esters are cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate, cellulose nitrate.

Cellulose ethers

Products of the etherification of certain of the hydroxyl groups of the cellulose macromolecule; the ethers are soluble in, or solubilized by, water and simple alcohols and find use as the basis of water-soluble adhesives for paper and as thickening agents in water-borne adhesives. *Note.* Examples of cellulose ethers are carboxymethyl cellulose, ethyl cellulose, methyl cellulose.

Cellulose gum

A water-soluble cellulose derivative used as a substitute for gum arabic (q.v.)

Chlorinated rubber

A white powder or fibrous product obtained by the controlled chlorination of natural rubber. *Note.* Chlorinated rubber is used as a compounding ingredient in adhesives.

Colophony

See 'rosin'.

Cyclized rubber

An isomeric derivative of natural rubber produced by a variety of chemical treatments. The products are resinous and are used as rubber-to-metal adhesives.

Dammar resin

Resin obtained from species of *Shorea*, *Hopea*, *Balnocarpus*, and which is soluble in certain organic solvents. *Note.* Dammar resin is used as a tackifier and modifier of pressure-sensitive adhesives.

Dextrin(e)

Modified starch prepared from starch by heat treatment in the dry state with or without the addition of small quantities of chemical agents. *Note.* Dextrine is used in certain water-borne adhesives.

Gum arabic

The dried exudation from the stem and branches of *Acacia senegal* Willdenow and other species of *Acacia*. High-purity varieties are known as 'gum acacia'.

Gum tragacanth

The dried mucilaginous exudation from *Astragalus gummifer* and other species of *Astragalus (Leguminosae)*, and which is partly soluble in water. *Note.* Gum tragacanth is used as a modifier and stabilizer in water- (or occasionally alcohol-) borne adhesives.

Linseed oil

Oil obtained from mature seeds of linseed (*Linum usitatissimum* L.) by expression or solvent extraction.

Oleo-resinous materials

Materials composed of vegetable drying oils in conjunction with resins that may be either natural or synthetic. *Note.* Oleo-resinous materials are used occasionally as adhesives for labels and transfers.

Rosin

A resin obtained as residue in the distillation of crude turpentine from the sap of the pine tree (gum rosin) or from an extract of the stumps and other parts of the tree (wood rosin); also called 'colophony'. *Note.* Hydrogenated and polymerized grades are available.

Rubber hydrochloride

The derivative of natural rubber products produced by the action of hydrogen chloride.

Soya bean protein

A protein derived from soya bean seeds. When compounded with other reactants, it is used as an adhesive, mostly in plywood.

Starch

Vegetable carbohydrate occurring in the granular form in certain plants and corresponding to a polymer composed almost exclusively of anhydroalpha-D-glucose groups.

Starch ester

Modified starch in which the hydroyxl groups of the starch have been totally or partially esterified.

Starch ether

Modified starch in which the hydroxyl groups of the starch have been totally or partially etherified.

Terpene resin

Pale thermoplastic polyterpene hydrocarbons obtained by the acid-catalyzed polymerization of the bicyclic monoterpene β-pinene (or occasionally α-pinene) products of the distillation of sulphate wood turpentine. *Note.* Terpene resin is principally used in adhesives as a tackifier (*see* 'solvent-borne adhesive').

Mineral origin

Acrylic

A general term used to describe a fairly large family of polymers and copolymers where at least one principal structural unit is derived from acrylic or methacrylic acids or their esters.

$$CH_2 = CH\ COOR . CH_2 = \underset{\underset{CH_3}{|}}{C}\text{–}COOR.$$

Note. Polymers of this class find outlets as constituents of many types of solvent-borne adhesives and emulsion adhesives, particularly where resistance to plasticizer migration is required.

Aminoplast

See 'amino-resin'.

Aminoplastic resin

See 'amino-resin'.

Amino-resin

A thermosetting synthetic resin derived from a condensation reaction of urea, thiourea, melamine or allied compounds alone or in combination, with formaldehyde; also called 'aminoplast', 'aminoplastic resin'.

Asphalt

See 'bitumen'.

Bitumen

A very viscous liquid or solid, consisting essentially of hydrocarbons and their derivatives, that are soluble in carbon disulphide. It is substantially non-volatile and softens gradually when heated. *Note.* Bitumen is black or brown in colour and possesses waterproofing and adhesive properties. Bitumen is obtained by refinery processes from petroleum, and is also found as a natural deposit or as a component of naturally occurring asphalt, in which it is associated with mineral water.

Chlorinated PVC

A granular material produced by the chlorination of polyvinyl chloride. It is soluble in a wide range of organic solvents. *Note.* Chlorinated PVC is used in adhesives for bonding plastics, particularly for bonding unplasticized polyvinyl chloride.

Chloroprene rubber (CR), polychloroprene

A range of synthetic rubbers based on polymerized chloroprene, widely used in the formulation of contact adhesives.

Chlorosulphonated polyethylene

A vulcanizable elastomeric material prepared by the simultaneous chlorination and chlorosulphonation of polyethylene in solution with gaseous chlorine and sulphur dioxide. *Note.* Chlorosulphonated polyethylene is used as a surface coating and in those applications where synthetic rubber is

typically used.

Coumarone/indene resin

A type of thermoplastic resin obtained by the acid catalyzed polymerization of coal-tar petroleum fractions rich in coumarone and indene. *Note.* Coumarone/indene resin is frequently used as a tackifier.

Cyanoacrylate monomer

A highly specialized type of acrylic monomer, esters of cyanoacrylic acid having the general formula

$$CH_2 = \underset{\underset{CN}{|}}{C}\text{–}COOR.$$

Note. Cyanoacrylate monomers are capable of polymerizing rapidly in the form of thin enclosed films and are used as the active entity in certain close-setting polymerizing adhesives.

Epoxide resin

A synthetic resin containing epoxide groups; also called 'epoxy resin'. *Note.* This is a class of thermosetting resin that may be used in adhesives for structural purposes especially when cross-linked with a hardener or catalyst such as, for example, amines or anhydrides.

Epoxy resin

See 'epoxide resin'.

Ester gum

Resinous esters of rosin acids with polyhydric alcohols such as glycerol or pentaerythritol. *Note.* Ester gums are sometimes used in tackifiers (q.v.).

Furane resin (furan)

A thermosetting synthetic resin derived from the condensation of a phenolic compound and furfural.

Melamine formaldehyde (MF)

See 'amino-resin'.

Nitrile/butadiene

See 'polybutadiene/acrylonitrile rubber'.

Novolak

The result of reacting phenols and aldehydes normally under alkaline conditions with aldehyde in molar excess. The molecules do not contain reactive methylol groups and cannot condense on the application of heat without the addition of hardening agents (*see also* 'resol').

Phenol formaldehyde (PF)

See 'phenolic resin'.

Phenolic resin

A synthetic resin produced by the condensation of a phenol (e.g. phenol, cresol, xylenol, resorcinol or mixtures of these compounds) with an aldehyde or mixtures of aldehydes (formaldehyde, furfuraldehyde) (*see also* 'resol' and 'novolak').

Polyacrylonitrile/butadiene/styrene (ABS)

A range of synthetic rubbers or resins made by the copolymerization of butadiene, acrylonitrile and styrene. They have oil, solvent and plasticizer-resistant properties depending on their acrylonitrile content.

Polyamide (PA)

The polymeric reaction product usually of dicarboxylic acids and diamines having the repeating linkage

$$\text{–}(R\text{–}\underset{\underset{H}{|}}{N}\text{–}\underset{\underset{O}{|}}{C}\text{–})$$

Note. There are 'unreactive' and 'reactive' types of polyamides. The former are made from dimer acids and diamines and are solids used as hot-melt adhesives. The latter are usually made from dimer acids and polyamines and contain free amine groups. They are usually liquids and are used in two-part adhesives. They are referred to as 'polyaminoamides'.

Polybutadiene/acrylonitrile rubber (nitrile rubber, NBR), nitrile/butadiene

A range of synthetic rubbers made by the copolymerization of butadiene and acrylonitrile. They have oil, solvent and plasticizer-resistant properties dependin on their acrylonitrile content.

Polybutadiene/styrene rubber (SBR), styrene/butadiene rubber

A range of general purpose synthetic rubbers or resins made by the copolymerization of butadiene and styrene. When suitably compounded they form the base for a wide range of solvent-borne adhesives. SBR is also available as latices which are constituents of many adhesives.

Polychloroprene, chloroprene rubber (CPR)

A range of synthetic rubbers based on polymerized chloroprene, widely used in the formulation of contact adhesives.

Polyester

Polymeric reaction product of alcohols and carboxylic acids having the repeating linkage

$$(\text{–}R\text{–}\underset{\underset{O}{|}}{C}\text{–}O)$$

The polyester may be of the saturated or unsaturated type depending on the dicarboxylic acid used. *Note.* The unsaturated polyesters are used in conjunction with a liquid unsaturated monomer (e.g. styrene) as the basis of two-part adhesives that require a catalyst system. The saturated polyesters are widely used as hot-melt adhesives.

Polyethylene (PE)

A polymer of ethylene, having the main chain repeat unit $\text{–}(CH_2\cdot CH_2)\text{–}$, used in hot-melt adhesive formulations.

Polyisobutylene (PIB)

A product of the polmerization of isobutylene (2 methylpropene) having the basic main chain repeat unit $\text{–}(CH_3)_2\ CH\text{–}$. *Note.* Polyisobutylene is sometimes used as a basis of solvent-borne adhesives giving films with pressure-sensitive or self-sealing properties, and as a modifier.

Polyolefin

A thermoplastic material produced by the polymerization or copolymerization of olefins, e.g. ethylene, propylene.

Polystyrene (PS)

A thermoplastic material produced by the polymerization of styrene. *Note.* Polystyrene is used in solution in organic solvent as an adhesive for polystyrene and certain porous materials.

Polysulphide

Polymers, usually liquids, containing disulphide linkages together with repeated bis(ethylene oxy)–methane groups. These groups are most commonly terminated with thiol and hydroxyl groups.

Polyurethane

A polymer derived from the reaction of a polyisocyanate with a polyhydroxyl compound normally of polyester or polyether structure.

Polyvinyl acetal

A thermoplastic material derived from polyvinyl acetate i., which ester groups have been replaced by hydroxyl groups and most of these hydroxyl groups converted to acetal groups by reaction with an aldehyde. *Note.* The term 'polyvinyl acetal' is used for the polymer made from acetaldehyd and generically for the other members of the series.

Polyvinyl acetate (PVAC)

A range of thermoplastic materials in either emulsion or resinous form produced by the polymerization of vinyl

acetate as the sole or principal monomer. *Note.* Polyvinyl acetate is used as a versatile adhesive for porous materials, particularly for wood and paper, and for general packaging work.

Polyvinyl alcohol (PVAL)

A thermoplastic material produced by the hydrolysis of polyvinyl acetate. Commercial polyvinyl alcohol usually contains some residual acetate groups. *Note.* The uses of polyvinyl alcohol are as follows: (a) as a water-soluble adhesive for porous materials and for use in contact with food; (b) as an additive in other adhesives to improve adhesion and as a stabilizer, etc.; (c) as a heat-seal or moisture-reactivation adhesive.

Polyvinyl butyral

A thermoplastic polymer made from polyvinyl alcohol and butyraldehyde. *Note.* The main uses of polyvinyl butyral are as follows: (a) as a constituent of two-polymer systems which provide high-strength structural adhesives; (b) as a main component of certain hot-melt adhesives used in particular for laminated safety glass and packaging applications.

Polyvinyl chloride (PVC)

A range of thermoplastic materials produced by the polymerization of vinyl chloride. *Note.* When compounded with suitable plasticizers, adhesion-promoting materials, stabilizers, etc., certain types of PVC form plastisols which may be used as flexible hot-setting adhesives. The uses of PVC are as follows. (a) Plastisols: gap-filling shock-absorbing adhesives. (b) In solution in certain organic solvents they provide adhesives for PVC and vinyl copolymer materials.

Polyvinyl formal

A thermoplastic polymer made from polyvinyl alcohol and formaldehyde. *Note.* The main use of polyvinyl formal is as a constituent of two-polymer systems to provide high-strength structural adhesives.

Resinoid

A thermosetting resin, either in the initial, temporary, fusible state or in the final, infusible state (*see also* 'novolak').

Resol

The result of reacting phenols and aldehydes normally under alkaline conditions with aldehyde in molar excess. The molecules contain reactive methylol groups which will condense together on the application of heat (*see also* 'novolak').

Resorcinol formaldehyde

See 'phenolic resin'.

Silicone polymer (SI)

A polymer in which the molecules consist of main chains of alternate silicon and oxygen atoms with side groups containing carbon.

Styrene/butadiene rubber

See 'polybutadiene/styrene rubber'.

Urea formaldehyde

See 'amino-resin'.

Vinyl resin

Resin based on the vinyl group or radical $CH_2 = CH-$. In combination with another group or radical R it may define a vinyl monomer $CH_2 = CH - R$, which can be converted, by addition reaction, to a polymer having the main chain repeat unit

$$-CH_2-\underset{\underset{R}{|}}{CH}-.$$

Note. Technological usage of vinyl resin is normally restricted to materials whose main chain repeat units are derived from vinyl chloride (where R is Cl), vinyl acetate (where R is CH_3COO-) or the theoretical vinyl alcohol (where R would be OH). Strict polymer science nomenclature would include any polymer derived from a monomer of the above general type, e.g. polystyrene.

Wax

A range of low molecular mass solid aliphatic hydrocarbons such as paraffin wax or microcrystalline wax commonly used in hot-melt adhesives.

ACKNOWLEDGEMENT

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CLEAR AND PIGMENTED EPOXY RESINS FOR STAINED GLASS CONSERVATION: LIGHT AGEING STUDIES

NORMAN H. TENNENT

Abstract—Daylight and accelerated ageing tests on a series of clear epoxy resins are described and the results discussed in terms of their tendency to yellow on exposure to light. Some factors important in the yellowing process are described. A series of dyestuffs which disperse easily in epoxy resin to give transparent casts with good light-fastness is reported.

1. INTRODUCTION

The conservation of stained glass panels often incorporates techniques which utilize synthetic resins for edge-to-edge jointing of broken glass or as fillers for replacing missing parts [1]. The problems encountered in selection of suitable materials for conservation of vitreous artifacts have been fully described by Moncrieff [2] and adhesives and fillers for ancient materials have been reported [3]. Epoxy resins have been used extensively as both adhesives and gap-fillers for glass conservation and a recent article describes their application to glass vessels [4]. For stained glass the resin can be pigmented to match the colour of the original glass [5, 6].

In many cases, however, epoxy resins are used as adhesives while other materials, notably acrylics, are used as gap-fillers [4, 7, 8]. The good resistance of acrylics to yellowing renders them suitable for this purpose but their poor adhesion to glass is a severe disadvantage. It was considered desirable as a starting point for the work described in this article that, if possible, a single material should function as both an adhesive and gap-filler for glass conservation, and epoxy resins were considered a prime candidate.

Although they have many suitable properties which render them an effective class of polymer for glass conservation, the propensity of many epoxy resins to yellow with age is a disadvantage. For industrial purposes, water-white clarity and non-yellowing characteristics are generally of low importance and these factors are subordinate to optimization of, for example, adhesive strength, chemical resistance or heat distortion temperature. Consequently, while thermal degradation of epoxy resins has been widely studied, their photodegradation—of greater importance to conservators—is poorly documented and little understood. Lee and Watson [9] have reported the ultraviolet resistance of several epoxy resin systems and the yellowing of epoxy resins for use as conservation materials has been briefly mentioned [3].

The light-fastness of dyes and pigments varies greatly. Furthermore this property depends on the resin medium [10] and it is meaningless to specify the light-fastness of a dyestuff without reference to the medium in which it is incorporated. The implication is that for conservation purposes, where the most stringent demands are made on durability, each dyestuff should be evaluated in the medium in which it will be used. Again epoxy resins have not been well studied in this respect and manufacturers do not generally quote the light-fastness of dyes and pigments in epoxy medium.

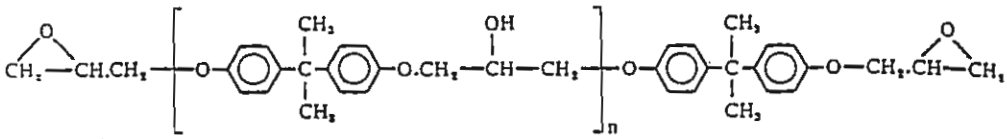
It is therefore the purpose of this article to report the ageing behaviour of epoxy resins currently used in glass conservation, to examine the potential of alternative water-white epoxy resins, and to suggest a range of dyestuffs suitable for pigmenting epoxy resins for glass conservation. Photochemical degradation can modify various polymer properties. This study is, however, concerned solely with the yellowing of clear epoxy resins and the fading of pigmented epoxies by the action of light.

2. SELECTION OF RESINS FOR INVESTIGATION

Epoxies are basically two-component systems consisting of a resin and hardener which react to form the cured product. The chemistry of epoxy resins has been well summarized by Potter [11]. Although epoxy resins can be grouped into a small number of sub-classes depending on the type of resin and hardener employed, many thousands of variations within these classes are available commercially. These variations lead to different physical and chemical properties such as temperature of cure, viscosity and working life of the mixture, or hardness and water-whiteness of the cured system. In addition, other components such as flexibilizers or accelerators may be added to the two main components to modify their properties.

The six products evaluated in this study and described in Table 1 were selected either because they are currently used for glass conservation or because it was felt they had potential in this connection. Selection for ageing studies was made primarily on the basis that the cured resin should possess water-white clarity. Since heating glass objects is inadvisable [12] the restriction to room-temperature cure served to eliminate very many products.

The resin component of all the products in this study is based on the diglycidylether of Bisphenol A (diphenylolpropane) and has the general formula:



Resins with a variety of molecular weights are possible and this is dependent on the number of repeat units, represented by different values of n. Ablebond 342-1, for example, is a low molecular weight resin where n is essentially 0 or 1, and predominantly 0.

The hardeners are all amines of various chemical constitutions.

3. SELECTION OF DYESTUFFS FOR INVESTIGATION

In order to produce coloured casts resembling stained glass, a range of dyes and pigments which disperse readily to give intense colours and good transparency is necessary. Many dyestuffs either do not disperse easily in epoxy resin or give opaque casts. Several products were excluded on these grounds alone. The problem is successfully overcome by the Chromophtal range in which the pigment is dispersed in dioctylphthalate (DOP) which promotes ready dispersion at room temperature. Table 3 lists the selected ranges whose hues are suitable for stained glass restoration.

4. DETERMINATION OF PHOTOCHEMICAL STABILITY

The epoxy resin samples were prepared as described below in two forms: as clear or coloured casts for visual and instrumental examination, and as thin films for instrumental examination by IR and UV-visible spectroscopy. The thickness of the casts was chosen to be representative of that encountered in stained glass panels.

Ageing was performed under accelerated conditions using the apparatus first reported by Giles, Shah, and Baillie [13] and now available commercially from Microscal. Two light sources—Philips 400 W MB/U and 500 W MBTL lamps—were used. This apparatus has been used extensively to determine the light-fastness of dyed textiles including dyestuffs for conservation [14]. The role of various factors in accelerated ageing tests has been sum-

marized by Feller [15]. A different balance of factors will operate in the photochemical deterioration of polymers (and indeed between different polymers [16]) compared to dyestuffs. Reliable extension of the Microscal apparatus to the degradation of polymers cannot therefore be inferred from success with dyed textiles. Thus, while the Microscal apparatus appears to offer a cheap, convenient and effective means of performing accelerated ageing tests on many conservation materials, the accelerated ageing tests in this study have been complemented by daylight ageing tests.

5. STANDARDS FOR DETERMINATION OF PHOTOCHEMICAL STABILITY

The light-fastness of dyed textiles is commonly specified with respect to eight ISO Blue Wool Standards and their application to dyes for conservation has been reported [14]. These standards also find application in the ageing of plastics [17] and Feller has suggested their adoption as standards for classification of thermoplastic resins for conservation [18]. A further use of these standards as monitors for illumination under museum conditions has been described [19].

In this study the ISO Blue Wool Standards have been used conventionally [20] to determine the light fastness of the pigmented epoxy resins (Table 3). They have also been incorporated into the ageing tests on the clear resins as dosimeters for the amount of radiation received. Although these standards are non-uniform in their response to radiation throughout the U[illegible] visible spectrum, good spacing of fading rates with MB/U and MBTL lamps compared [illegible] daylight [13] would give confidence to their use as simple dosimeters to enable intercomparison between daylight and accelerated ageing tests. Furthermore, the end point of the tests was taken as the onset of just perceptible fading of Standard 7, which is faded solely by radiation less than 460 nm [21], the region causing most degradation in polymers.

6. EXPERIMENTAL

6.1 *Preparation of Clear Resins*

Casts. 50 g samples of resin were mixed with hardeners and, where necessary, additional components according to the manufacturer's recommended proportions as detailed in Table 1. Quantities were measured precisely in disposable polypropylene beakers and the

TABLE 1

Epoxy system		*Constituents*	*Mixing proportions*
Araldite AY103/HY951	AY103:	Bisphenol A diglycidyl ether + dibutylphthalate	100
	HY951:	Triethylene tetramine	10
Plastogen EP	Resin:	Bisphenol A diglycidyl ether + dibutylphthalate	100
	Hardener:	Aliphatic amine	33
Thermoset 600/No. 64 + Accelerator	600:	Bisphenol A diglycidyl ether	100
	No. 64:	$NH_2CH(CH_3)CH_2-[OCH_2CH(CH_3)-]_xNH_2$	35
	Accelerator:	Alkyl phenol, $C_9H_{19}.C_6H_5OH$	15
Epotek 301	Resin:	Bisphenol A diglycidyl ether	100
	Hardener:	Aliphatic amine	25
Araldite MY790/X83-319 + Flexibilizer DY040	MY790:	Bisphenol A diglycidyl ether	100
	X83-319:	Isophorone diamine	24
	DY040:	Polypropylene glycol	20
bond 342-1	Resin:	Bisphenol A diglycidyl ether	100
	Hardener:	Polyoxypropylene diamine	32

mixtures stirred with a glass rod. Casts of dimensions 5 × 2·5 × 0·3 cm were prepared in silicone rubber (Silastic 9161 RTV/Catalyst N9162) moulds. Mild warming of Araldite MY790 and Ablebond 342-1 resins was necessary since these resins were solid at room temperature.

Thin Films. Samples of the mixed resin system were pressed between smooth rigid polythene sheets and cured under a heavy load to ensure thin films. The films were removed from the polythene with a scalpel and mounted on Specacard holders for spectroscopic examination. Uniformity of thickness between samples was gauged by the intensity of the IR absorption bands.

6.2. *Preparation of Pigmented Resin*
The colouring agents (0·05 % by weight of the total resin system) were added to 50 g resin samples (Ablebond 342-1 and Thermoset 600/ No. 64) and dispersed by stirring thoroughly with a glass rod, and when necessary warming at 50°C, prior to addition of the hardener and other components. Adjustment of the weight of the Chromophtal DOP Paste range was made to compensate for the presence of plasticizer. Casts of dimensions 5 × 2·5 × 0·3 cm were prepared in silicone rubber moulds.

6.3. *Ageing Tests*
Daylight Exposure. Exposure to daylight was carried out under glass in an exposure rack which incorporated the essential features prescribed by BS 1006: 1971 [20]. The exposure rack faced due south and samples were disposed at an angle of 56°, the latitude of Glasgow, the location of the test site.

Microscal Exposure. This apparatus was used with water-cooled cells which maintained the sample temperature below 50°C (MB/U lamp) and 40°C (MBTL lamp) as measured by Hermet temperature-sensitive strips. The relative humidity was maintained at about 45 % by saturated solutions of potassium carbonate in the sample cells. Exposure was continued till ISO Blue Wool Standard 7 displayed just perceptible fading. This was equivalent to approximately 600 hours and 1000 hours illumination for the MB/U and MBTL lamps respectively.

Samples. The clear resin casts were covered to half their width with aluminium foil and placed on a backing of aluminium foil. Removal of the foil after exposure allowed measurement of the extent of yellowing. The thin films were exposed with a backing of aluminium foil. The coloured casts were progressively covered by strips of aluminium foil in accord with the method of test BS 1006: 1971.

6.4 *Assessment of Samples from Ageing Tests*
Yellowness Index. The Yellowness Indices were determined according to the prescribe method [22] by means of a Pretema Spectromat FS3A.

Spectroscopic Examination. IR spectra were recorded on a Perkin Elmer PE297 instrument and UV-visible spectra were recorded on a Pye Unicam SP8-100 recording spectrophotometer.

Visual Inspection. Grey Scale Contrast and Light-fastness ratings were estimated by a panel of three observers under artificial daylight illumination (conforming to BS 950 Part 1) against a standard white tile background.

7. RESULTS AND DISCUSSION

The light ageing tests resulted in varying degrees of yellowing of the clear epoxy resin samples and served to discriminate well between those products which maintained good water-white clarity and those which yellowed badly. In each case the yellowing occurred predominantly on the top surface of the resin casts.

The light-fastness tests on the pigmented resins revealed a very wide variation in this property in epoxy resin medium and enabled selection of suitable products.

7.1. *Clear Resins*

7.1.1. *Yellowness Index of Resin Casts*

The relative photostability of the clear resins may be gauged from Table 2 which categorizes the resins in terms of their Yellowness Index [22] before and after daylight and Microscal (MB/U) ageing. Similar results were obtained in Microscal (MBTL) ageing tests. The Yellowness Index* is used in this study as a quantitative measure of both the intrinsic yellowness of the sample and the degree of yellowing produced by ageing. Resins with a strong yellow tint will have a high Yellowness Index whereas resins which approach water-white clarity will have low values.

TABLE 2

Epoxy resin	*Yellowness index*						*Grey scale contrast*	
	Daylight			*Microscal MB/U*			*Daylight*	*Microscal MB/U*
	Before ageing	*After ageing*	*ΔYI*	*Before ageing*	*After ageing*	*ΔYI*		
Araldite AY103/HY951	35·1	82·4	47·3	30·6	89·7	59·1	3	2/3
Bestogen EP	23·4	68·2	44·8	23·0	77·7	54·7	3	3
Thermoset 600/No. 64 (+Accelerator)	14·8	34·8	20·0	10·7	35·8	25·1	4	3/4
Epotek 301	15·0	21·2	6·2	15·1	21·7	6·6	4/5-5	4/5
Araldite MY790/X83-319 (+Flexibilizer DY040)	10·0	21·5	11·5	10·1	15·3	5·2	4/5	4/5-5
Thermoset 600/No. 64	11·5	17·6	6·1	9·1	13·7	4·6	4/5-5	4/5-5
Ablebond 342-1	10·1	15·9	5·8	8·0	13·0	5·0	4/5-5	4/5-5

Thus it can be seen from Table 2 that the resins before ageing show varying degrees of yellowness and that the increase in yellowness on ageing also varies greatly. Araldite AY103/HY951, for example, has a strong yellow tint which darkens dramatically on prolonged exposure to light. This yellowing is represented by a change in Yellowness Index, ΔYI, of 47·3 (daylight) and 59·1 (Microscal MB/U). In contrast, Ablebond 342-1 yellows just perceptibly on exposure to the same conditions reflected by ΔYI values of 5·8 (daylight) and 5·0 (Microscal MB/U). Indeed this resin is markedly less yellow after exposure than Araldite AY103/HY951 before exposure.

It is a further feature of Table 2 that the results of exposure in the Microscal apparatus compare well with those from daylight exposure. The seven resins show the same order of

*The Yellowness Index, YI, is defined as follows:

$$YI = (100\,(1{\cdot}28X_{CIE} - 1{\cdot}06Z_{CIE}))/Y_{CIE}$$

where X_{CIE}, Y_{CIE} and Z_{CIE} are the tristimulus values of the specimen relative to source C.

resistance to yellowing in each test. In addition, although the absolute values of the Yellowness Index are affected by minor imperfections in the quality of the casts, there is good correlation between the values of ΔYI for the different exposure conditions. The figures do indicate, however, increased yellowing of Araldite AY103/HY951 and Plastogen EP samples as a result of Microscal exposure. The presence of prominent lines below 450 nm in the emission spectrum of MB/U and MBTL lamps [13] may be responsible for the enhancement of yellowing over daylight exposure in these cases. Further work is in progress to examine the variation between Microscal and daylight exposure.

The participation of thermal degradation in the yellowing process was excluded by a control set of resin casts which showed no discernible yellowing when maintained in the dark at 50°C, the operating temperature of the Microscal apparatus, for the duration of the tests.

7.1.2. *Grey Scale Contrast of Resin Casts*

The degree of fading of textile samples is often expressed in terms of the contrasts of the ISO Grey Scale for Assessing Change in Colour (BS 2662) and this scale has been well described by Feller [19]. The degree of yellowing of the aged epoxy samples can also be quantified in the same way but for this the Grey Scale for Assessing Staining (BS 2663) was preferred [23]. The contrast between white and grey in this scale facilitates comparison with the clear and yellow portions of the aged samples. The division of this scale into half steps is an additional advantage. The scale is marked in half steps from 1 (greatest contrast) to 5 (no contrast) and the results of grading in these terms are given in Table 2. Good discrimination is possible by this simple visual method which correlates surprisingly well with ΔYI, an instrumental expression of the same feature.

It is clear from these results that three resins, Nos. 5–7 in Table 2, approach the ideal of water-white clarity and retain this property well after ageing. As such they would be categorized as Class A materials in Feller's designation of museum conservation materials [15]. Ablebond 342-1 has performed particularly well in practice and the application of this resin to stained glass conservation will be described in a future article.

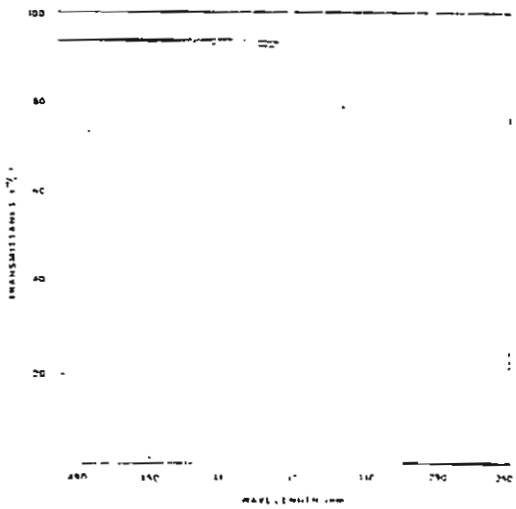


FIG. 1 UV-visible transmission spectra of Araldite AY103/HY951 (1) before ageing, (2) after 200 hours, (3) after 400 hours, (4) after 600 hours' Microscal (MB/U) ageing.

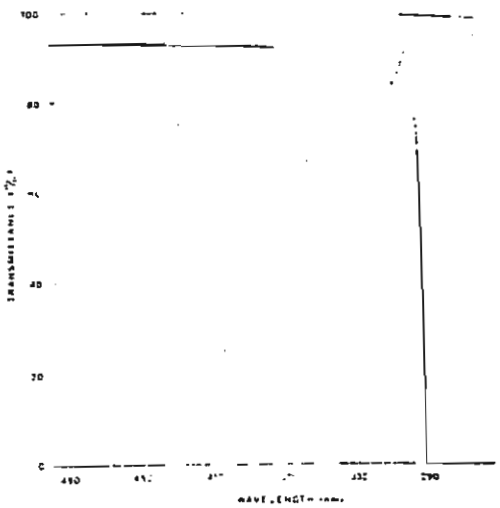


FIG. 2 UV-visible transmission spectra of Ablebond 342-1 (1) before ageing, (2) after 200 hours, (3) after 400 hours, (4) after 600 hours' Microscal (MB/U) ageing.

1.3. *UV-visible and IR Spectra of Thin Resin Films*

The degradation of the resins was monitored by UV-visible and IR spectroscopy.

The UV-visible spectra were recorded at intervals of 200 hours' exposure to the MB/U lamp and show quantitatively the spectroscopic changes which are seen as yellowing by the naked eye. Again the pronounced yellowing of Araldite AY103/HY951 is clear from the marked shift of the spectrum towards the visible accompanied by increasing absorption in the blue region as ageing proceeds. In contrast, the spectra of Ablebond 342-1 show very little change, indicative of the good photostability of this system. These spectra are reproduced in Figures 1 and 2. Again no thermal degradation was detected under these test conditions.

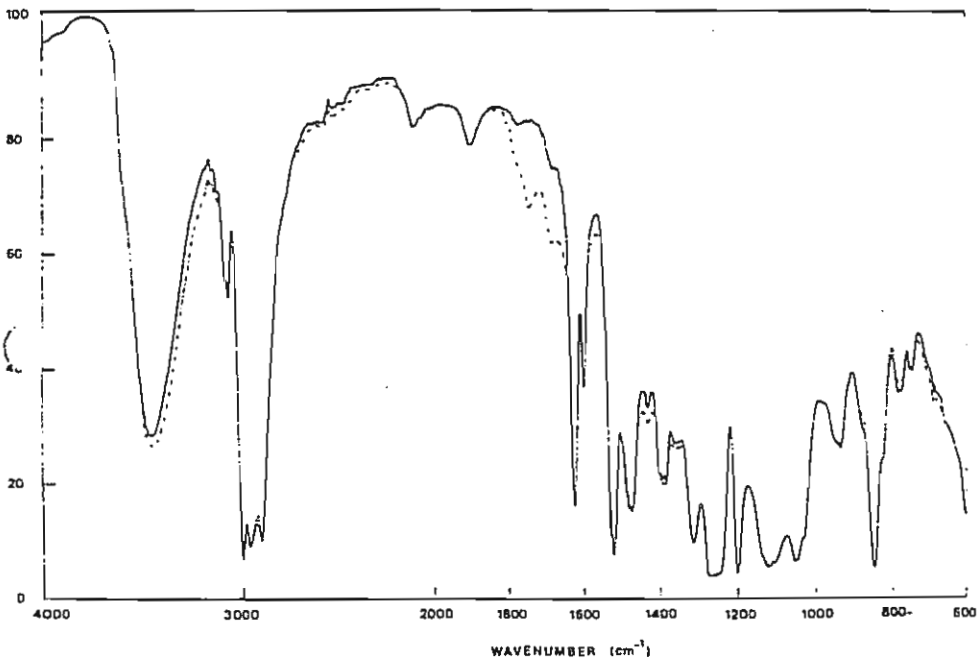


FIG. 3 Infrared absorption spectrum of Ablebond 342-1. Before ageing (——). After ageing (·—·—·—·).

The IR spectra of all seven resins under investigation have been recorded at intervals throughout the exposure tests. Similar changes are observed in all cases though they do not appear to be quantitatively related to the degree of yellowing. Figure 3 shows the IR spectrum of Ablebond 342-1 before and after ageing. From this the principal chemical changes which accompany the yellowing can be deduced, the most pronounced of which is the formation of carbonyl bonds (C=O) characterized by new bands at 1725 and 1660 cm^{-1}. The growth of the 1725 cm^{-1} band in Araldite AY103/HY951 (Figure 4) is partially obscured by the carbonyl absorption of dibutylphthalate plasticizer.

In addition, the position of the hydroxyl (OH) stretching band has shifted slightly to higher wavelength at 3425 cm^{-1}. There is a slight increase in intensity and the band has broadened. Less pronounced is a slight diminution in the intensity of the band at 918 cm^{-1}. Cure of the resin is accompanied by the disappearance of a band at 910 cm^{-1}, characteristic of the epoxide ring [24]. The change in this region after ageing may therefore be indicative of ring opening of some residual epoxide groups.

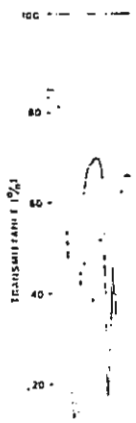


FIG. 4 Infrared absorption spectrum of Araldite AY103/HY951 in the carbony region. Before ageing (——). After ageing (·—·—·).

From these spectra the degradation is, as would be expected, seen to be an oxidative proces The precise mechanism of photodegradation is uncertain and is the subject of furthe investigation. Many factors are likely to be important not least of which is the chemica nature of the resin and hardener. From this study, however, it is clear that additional factor are important in the yellowing process.

7.1.4. *Factors Affecting the Yellowing of the Resin*

(i) *Purity of the Resin*

The presence of additives such as plasticizers, diluents and accelerators is common in epox resin technology. That these resins can promote yellowing is clear from this study wher dibutylphthalate plasticizer and alkyl phenol accelerator both promote the yellowing of th systems to which they are added (Table 2).

Ageing of Araldite AY105/HY951, identical to the AY103/HY951 system except for th presence of 20% dibutylphthalate in the latter, shows that the presence of plasticize promotes the yellowing significantly. Addition of 20% dibutylphthalate to the AY10 HY951 and Ablebond 342-1 systems causes enhanced yellowing of these resins. Since th plasticizer undergoes no yellowing under the same conditions, an intermolecular interactio leading to the yellowing can be inferred. The role of trace impurities is also thought to important and this factor is the subject of a further study.

(ii) *Ratio of Resin to Hardener*

Casts of Ablebond 342-1 resin with 25% excess or deficiency of hardener from the manu facturer's recommended value showed more yellowing than normal casts. The yellowin was more pronounced in the sample with hardener deficiency. In contrast, Aral AY103/HY951 showed less pronounced yellowing when 25% excess of hardener was prese compared to casts with the recommended proportions.

The effect is clearly variable and demands accurate measurement of resin and hardener b the conservator.

7.2. *Pigmented Resins*

It is a complementary part of this investigation that a range of suitable dyes and pigmen be selected which when added to epoxy resin disperse readily to produce transparent cas of good light-fastness. Table 3 lists a range of products which meet these requirement

TABLE 3

SELECTED DYESTUFFS SUITABLE FOR EPOXY RESINS

Dyestuff	*Supplier*	*Colour Index generic name*	*Chemical class*	*Light-fastness*			*Remarks*
				Day-light	*Micro-scal MB/U*	*Micro-scal MBTL*	
Chromophtal Yellow 3G DOP Paste	Ciba-Geigy	Pigment Yellow 93	Azo	8	8	8	25% pigment dispersion in DOP. Slightly cloudy casts
Thermoplast Yellow GS	BASF	Solvent Yellow 128	Quinophthalone	8	8	8	Mild warming in resin aids dispersion
Thermoplast Yellow G	BASF	Solvent Yellow 93	Monomethine	8	8	8	Mild warming in resin aids dispersion
Sudan Yellow 3G	BASF	Solvent Yellow 16	Azo	8	8	8	Disperses well in resin at room temperature
Oracet Yellow GN	Ciba-Geigy	Solvent Yellow 23	Azo	8	8	8	Disperses well in resin at room temperature
Orasol Orange G	Ciba-Geigy	Solvent Orange 11	Azo (Co complex 1:2)	6D	6-7D	7D	Disperses well in hardener at room temperature. Better light-fastness recorded with transmitted light
Orasol Red B	Ciba-Geigy	Solvent Red 7	Azo (Cr complex 1:2)	6D	5D	6-7D	Mild warming in resin aids dispersion. Better light-fastness recorded with transmitted light
Neozapon Bordeaux B	BASF	Solvent Red 118	Azo (Co complex 1:2)	8	8	8	Disperses well in hardener at room temperature
Chromophtal Violet B DOP Paste	Ciba-Geigy	Pigment Violet 37	Dioxazine	8	8	8	30% pigment dispersion in DOP
Chromophtal Blue A3R DOP Paste	Ciba-Geigy	Pigment Blue 60	Indanthrone	7	7 8	7-8	20% pigment dispersion in DOP
Chromophtal Blue 4GN DOP Paste	Ciba-Geigy	Pigment Blue 15:3	Beta-phthalocyanine	8	8	8	25% pigment dispersion in DOP
Chromophtal Green GF DOP Paste	Ciba-Geigy	Pigment Green 7	Polychloro-phthalocyanine	6D	6D	7D	25% pigment dispersion in DOP. Better light-fastness recorded with transmitted light
Irgalite Dispersed Black 1105	Ciba-Geigy	Pigment Black 7	Carbon Black	8	8	8	20% pigment dispersion in DOP

The light-fastness is specified in relation to the eight ISO Blue Wool Standards and in eac case falls in the range 6–8. As such they are suitable for conservation purposes.
The light-fastness tests were carried out on coloured epoxy casts prepared as describe above. Since the light-fastness of a given dye depends on the dye concentration and th thickness of the medium, these factors were kept constant from one cast to another. Thr exposure conditions were used: natural daylight, Microscal (MB/U) and Microscal (MBTL There is very good agreement between the results of daylight and Microscal exposure. accord with the observations for dyed textile samples. This is, however, the first report of th use of this apparatus in specifying the light-fastness of coloured resin samples.
These tests are necessitated by the variation in light-fastness which can occur with bindir medium [10]. In this study many dyestuffs were found to exhibit very poor light-fastness epoxy resin compared to polyester and acrylic resins. These results will be reported els where and one example will serve to illustrate the point. Thermoplast Blue P (Solver Violet 13), an anthraquinone derivative, displayed the highest light-fastness, 8, whe dispersed in acrylic resin and subjected to Microscal MB/U exposure. When dispersed epoxy resin, the lowest light-fastness, 1D, was recorded, and this dyestuff would darke after a few days exposure to natural daylight.
Ease of dispersion is a further problem and again is dependent on the resin system. It unfortunately true that dyes tend to disperse with ease but to have lower light-fastness tha pigments which disperse with difficulty. Immediate dispersion of the Chromophtal range pigments is possible and while large proportions of dibutylphthalate have been shown increase the yellowing of epoxy resin, the very small amounts of dioctylphthalate introduce into the resin mixture in this way do not seem to be disadvantageous. For some dyes, gent warming in the resin or hardener or resin/hardener mixture facilitates dispersion. Solubili in the hardener is generally greater than in the resin.
The addition of dyes or pigments can accelerate or retard the cure of resin systems. This wa not found with the materials investigated in this study.

8. CONCLUSION

Light ageing tests have shown that the yellowing commonly exhibited by epoxy resins nee not be a barrier to their use in glass conservation. Room-temperature curing systems whic maintain good water-white clarity can be found. Similarly, while epoxy resins are found t be a particularly harsh medium for ensuring good light-fastness, suitable colouring agen can be selected.
Examples of resins and dyestuffs are therefore suggested which on the basis of the behaviour to light satisfy the stringent demands made on conservation materials. Thes materials have been selected for application to stained glass conservation but the application to conservation of other materials, notably ceramics, would be justified on th basis of this work.

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SUPPLIERS OF MATERIALS AND EQUIPMENT

Epoxy Resins/Hardeners

Araldite. Ciba-Geigy Plastics and Additives Co., Plastics Division. Duxford, Cambridge CB2 4QA. UK.

Plastogen. Manufacturer: Alfons Schmidt. Speyer, St German-Str. 14, Germany. UK Supplier: Frank W. Joel Ltd. PO Box No. 6, Downham Market. Norfolk PE38 9ED.

Epotek. Manufacturer: Epoxy Technology Inc., 65 Grove Street, Watertown. Mass. 02172. USA. UK Supplier: Alpha Metals Ltd, 457 Kingston Road. Ewell. Surrey.

Thermoset. Manufacturer: Thermoset Plastics Inc.. 5101 East 65th Street, Indianapolis, Indiana 46220. USA. UK Supplier: Kentron International Ltd. Metropolitan House. Victoria Avenue. Southend-on-Sea, Essex SS2 6BS.

Ablebond. Manufacturer: Ablestik Laboratories. 833 West 182nd Street, Gardena. California 90248. USA. UK Supplier: Intersem Ltd. Haywood House, Pinner. Middlesex HA5 5QA.

Dyes/Pigments

BASF, Dispersions and Pigments Division, PO Box 4, Earl Road. Cheadle Hume, Cheadle, Cheshire SK8 6QG, UK.

Ciba-Geigy Plastics and Additives Co., Pigments Division, Roundthorn Industrial Estate. Wythenshawe. Manchester M23 9ND. UK.

Miscellaneous

Silastic 9161 RTV, Catalyst N9162. Dow Corning Ltd. Barry, Glamorgan. UK.

Heat Temperature Indicators. PJD Instruments Ltd, 15 The Green, Southall, Middlesex UB2 4AH, UK.

Specacards. Specac, Lagoon Road, St Mary Cray, Orpington. Kent BR5 3QX, UK.

Microscal Light-Fastness Tester. Microscal Ltd, 79 Southern Row. Kensal Rise. London W10 5AL. UK.

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Abstrait—On décrit des essais à la lumière du jour et en vieillissement accéléré d'une série de résines époxy transparentes et les résultats sont discutés en termes de jaunissement à la lumière. On y trouvera la description des facteurs importants de ce jaunissement ainsi que des données relatives à une série de colorants se dispersant facilement dans la résine époxy et conduisant à des moulages transparents dont on donne les différentes tenues à la lumière.

Kurzfassung—Tageslicht- und beschleunigte Alterungsteste an einer Reihe klarer Epoxydharze werden beschrieben und die Ergebnisse hinsichtlich ihrer Tendenz zur Vergilbung, wenn sie Licht ausgseetzt werden, diskutiert. Über eine Reihe von Farbstoffen, die sich leicht in Expoxydharz auflösen, um durchsichtige Güsse mit guter Lichtbeständigkeit zu ergeben, wird berichtet.